HYDROCRACKING CATALYST, PRODUCING METHOD THEREOF, AND HYDROCRACKING METHOD

Publication number: WO0012213
Publication date: 2000-03-09
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Classification:
- international: ***B01J23/85; B01J29/16; B01J35/10; B01J37/00; C10G45/08; C10G47/12; C10G47/14;*** *B01J21/12; B01J23/888; B01J29/14;* **B01J23/76; B01J29/00; B01J35/00; B01J37/00; C10G45/02; C10G47/00;** B01J21/00; (IPC1-7): B01J35/10; C10G47/12
- european: B01J23/85; B01J35/10; C10G45/08; C10G47/12
Application number: WO1999JP04722 19990831
Priority number(s): JP19980246458 19980901

Also published as:

EP1027156 (A
US6551500 (B
GC0000065 (A
EP1027156 (A
EP1027156 (B

Cited documents:

US5393409
GB2087747
US5435908
DE2817839
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Abstract of **WO0012213**

A hydrocracking catalyst has a carrier that has particles of a compound oxide and a binder present between these particles, and at least one metal component selected from Group 6, Group 9 or Group 10 of the Periodic Table supported on the carrier. The catalyst has a median pore diameter of 40 to 100 ANGSTROM and the volume of pores whose pore diameter falls within a range of 40 to 100 ANGSTROI is at least 0.1 mL/g. Moreover, the volume of pores of the catalyst whose pore diameter falls within a range of 0.05 to 5 mu m is 0.05 to 0.5 mL/g, and the volume of pores whose pore diameter is 0.5 to 10 m m is less than 0.05 mL/g. This catalyst is mechanically strong enough for practical use and has a high conversion rate and middle distillate selectivity in hydrocracking of hydrocarbon oils, particularly vacuum gas oil.

CLAIMS

[Claim(s)]
[Claim 1] The support which has the binder part which exists between the particle of a multiple oxide, and its particle, It is the hydrocracking catalyst which has at least one sort of metal components chosen from the 6th group, the 9th group, and the 10th group of the periodic table supported by the above-mentioned support. The central pore diameter of the above-mentioned catalyst is 40-100A, and the volume of the pore of the range which is the pore diameter of 40-100A is 0.1 mL/g at least. The hydrocracking catalyst whose volume of the pore which is the pore diameter of 0.5-10 micrometers the volume of the pore of the range of 0.05-0.5-micrometer pore diameter of the above-mentioned catalyst is 0.05 - 0.5 mL/g, and is less than 0.05 mL/g.
[Claim 2] The hydrocracking catalyst according to claim 1 by which the above-mentioned multiple oxide is constituted from at least one sort of multiple oxides chosen from a silica alumina, a silica-titania, a silica-zirconia, a silica-magnesia, a silica-alumina-titania, and a silica-alumina-zirconia.
[Claim 3] The hydrocracking catalyst according to claim 1 by which the above-mentioned multiple oxide is constituted from at least one sort of multiple oxides chosen from a silica alumina, a silica-titania, a silica-zirconia, a silica-magnesia, a silica-alumina-titania, and a silica-alumina-zirconia, and a USY zeolite.
[Claim 4] A hydrocracking catalyst given in any 1 term of claims 1-3 by which the above-mentioned binder part is constituted from at least one sort of an alumina and a boria-alumina.
[Claim 5] At least 60% of the particle of the above-mentioned multiple oxide is a hydrocracking catalyst given in any 1 term of claims 1-3 whose diameters are 10 micrometers or less.
[Claim 6] The hydrocracking catalyst according to claim 1 for hydrocracking the hydrocarbon oil which contains the fraction which has the boiling point 250 degrees C or more 80% of the weight or more.
[Claim 7] A hydrocracking catalyst according to claim 1 or 6 for the amount of [a part for vanadium and] nickel to hydrocrack the hydrocarbon oil which is 0.0005 or less % of the weight, respectively.
[Claim 8] A hydrocracking catalyst given in rare ******** 7 which the above-mentioned hydrocarbon oil is a vacuum gas oil, and is included by the amount of [a part for vanadium, and] nickel at 0.0001 or less % of the weight in a vacuum gas oil, respectively.
[Claim 9] The hydrocracking catalyst according to claim 1 whose central pole diameter of the above-mentioned catalyst is 50-85A.
[Claim 10] The hydrocracking catalyst according to claim 1 whose volume of the pore of the range of the 40-100A above-mentioned pore diameter is at least 0.15 - 0.6 mL/g.
[Claim 11] A hydrocracking catalyst given in any 1 term of claims 1, 9, and 10 whose volume of the pore of the range of the 0.05-0.5-micrometer above-mentioned pore diameter is 0.05 - 0.13 mL/g.
[Claim 12] The hydrocracking catalyst according to claim 11 characterized by the volume of pore with an above-mentioned pore diameter of 0.5-10 micrometers being less than 0.01 mL/g.
[Claim 13] It is the manufacture approach of a hydrocracking catalyst according to claim 1. The multiple oxide fine particles and the binder with which a diameter contains floc 10 micrometers or less at least 60% of the weight are mixed. The mixture of fine particles and a binder is fabricated, dried and

calcinated, and support is formed. The manufacture approach of the hydrocracking catalyst characterized by supporting at least one sort of metal components chosen as the above-mentioned support from the 6th group, the 9th group, and the 10th group of the periodic table.
[Claim 14] The manufacture approach of a hydrocracking catalyst according to claim 13 that the above-mentioned multiple oxide fine particles consist of at least one sort chosen from a silica alumina, a silica-titania, a silica-zirconia, a silica-magnesia, a silica-alumina-titania, and a silica-alumina-zirconia.
[Claim 15] The manufacture approach of a hydrocracking catalyst according to claim 13 that the above-mentioned multiple oxide fine particles consist of at least one sort chosen from a silica alumina, a silica-titania, a silica-zirconia, a silica-magnesia, a silica-alumina-titania, and a silica-alumina-zirconia, and a USY zeolite.
[Claim 16] The manufacture approach of a hydrocracking catalyst given in any 1 term of claims 13-15 by which the above-mentioned binder component is constituted from at least one sort of aluminum hydration oxide and boria content aluminum hydration oxide.
[Claim 17] The manufacture approach of a hydrocracking catalyst given in any 1 term of claims 13-15 in the range whose central pore diameter of a multiple oxide is 35-100A.
[Claim 18] The hydrocracking approach of the hydrocarbon oil characterized by changing into the product which decreased the fraction which is contained in the above-mentioned hydrocarbon oil by contacting a hydrocarbon oil for a hydrocracking catalyst according to claim 1 under existence of hydrogen, and which has the high boiling point relatively.
[Claim 19] The hydrocracking approach according to claim 18 characterized by being the hydrocarbon oil with which the above-mentioned hydrocarbon oil contains the fraction which has the boiling point 250 degrees C or more 80% of the weight or more.
[Claim 20] The hydrocracking approach according to claim 18 or 19 that the amount of [a part for the vanadium contained in the above-mentioned hydrocarbon oil and] nickel is 0.0005 or less % of the weight, respectively.
[Claim 21] The hydrocracking approach according to claim 20 that the above-mentioned hydrocarbon oil is a vacuum gas oil, and the amount of [a part for the vanadium contained in the vacuum gas oil concerned and] nickel is 0.0001 or less % of the weight, respectively.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
Field this invention of invention relates to the catalyst used for the hydrocracking approach list of a hydrocarbon oil suitable for the hydrocracking approach of a hydrocarbon oil, and its manufacture approach. Especially this invention relates to the catalyst used for the hydrocracking approach list which can hydrocrack a vacuum-gas-oil fraction efficiently and can be made to convert into light oil suitable for the hydrocracking approach of a vacuum-gas-oil fraction, and its manufacture approach.
[0002]
Background technique The need of the latest petroleum is in light ******. Although it is possible to aim at production increase by fluid bed catalytic cracking about a gasoline or naphtha, as for the kerosene called a middle cut, gas oil, jet fuel, etc., the thing of desirable quality is not obtained by fluid bed catalytic cracking. For this reason, in petroleum-refining industry, the approach of often hydrocracking a vacuum gas oil for production increase of a quality middle cut is used.
[0003]
Although the target fraction can be obtained in hydrocracking of a vacuum gas oil by contacting stock oil and a catalyst at an elevated temperature under a high-pressure hydrogen existence, the reaction condition for it and selection of a catalyst are important. For example, what is necessary is just to use the catalyst which supported the hydrogenation active metal kind for the support which makes a reaction condition severer or contains more strong zeolites of solid acid nature, in order to gather an invert ratio. However, although an invert ratio will become high if it is made to react using such a catalyst, gas and naphtha generate so much and there is a fault that the selectivity of a middle cut worsens.
[0004]
Then, in the design of the catalyst which produces a middle cut efficiently, attention is paid to the pore volume distribution of a catalyst in consideration of the diffusibility of the hydrocarbon molecule which reacts (Julius Scherzer, A.J.Gruia, "HYDROCRACKING SCIENCE AND TECHNOLOGY" Mercel Dekker, Inc., New York, 1996). For example, in the hydrocracking catalyst which supported the hydrogenation active metal with JP,6-190278,A to the support which consists of boria, a silica, and an alumina, it is indicated that it is suitable for that whose average pore diameter is 90-120A to acquire high middle-cut selectivity. Thus, raising middle-cut selectivity is the technique known for this field by taking into consideration the so-called pore volume distribution of meso pore.
[0005]
The hydrocracking catalyst which fills up the reactor of a fixed-bed circulation type and is used industrially on the other hand is usually fabricated the shape of a cylinder, and in the shape of a ball. The technique of making the so-called macro pore 0.05 micrometers or more existing in such a shaping catalyst is also known. For example, JP,5-36099,B is indicating the catalyst which makes the support which consists of an alumina system inorganic oxide and a zeolite come to support a hydrogenation active ingredient, in order to carry out the hydrogen treating of heavy hydrocarbon mainly like ordinary pressure residual oil. In this official report, since this catalyst has 0.1 or more mL/g of macro pores with

a pore diameter of 600A or more, it is indicated self-possessed and that can prevent lock out of the pore by it and a LGT gas oil yield is improved [of a carbonaceous-material metallurgy group contamination] as a result.

[0006]

However, it has the fault of being easy to produce the problem resulting from a catalyst breaking during reaction implementation or generally powdering it in case a mechanical strength becomes low (the Shirasaki quantity **, Kodansha edited "catalyst preparation" by Naoyuki Todo, 1974), and manufactures a catalyst and the shaping catalyst which has macro pore fills up a reactor with a catalyst, since voidage becomes high. As far as this invention person gets to know, the pore volume distribution of specific meso pore and the pore volume distribution of specific macro pore are introduced into a hydrocracking catalyst at coincidence, and a hydrocarbon oil, the hydrocarbon oil demetallization-ized while the fraction more than the predetermined boiling point was mainly included preferably, and especially the technique that used the hydrocracking catalyst concerning hydrocracking of a vacuum gas oil or heavy gas oil do not exist until now.

[0007]

Indication of invention The purpose of this invention has the selectivity of an invert ratio and a middle cut in offering the hydrocracking approach which used the hydrocracking catalyst for the new hydrocracking catalyst which has a practical mechanical strength highly, and its manufacture approach list in hydrocracking of hydrocarbon oil, especially a vacuum gas oil and heavy gas oil.

[0008]

The hydrocracking catalyst of this invention is a hydrocracking catalyst containing the catalyst support which has the binder part which exists between the particle of a multiple oxide, and its particle, and at least one sort of metal components chosen from the 6th group of the periodic table, the 9th group, and the 10th group, the central pore diameter of (A) this catalyst is 40-100A, and the pore volume of the range which is the pore diameter of 40-100A is 0.1 mL/g at least.;

(B) It is characterized by for the pore volume of the range of 0.05-0.5-micrometer pore diameter of this catalyst being 0.05 - 0.5 mL/g, and the pore volume which is the pore diameter of 0.5-10 micrometers being less than 0.05 mL/g.

[0009]

It is desirable that a multiple oxide consists of one sort chosen from a silica alumina, a silica-titania, a silica-zirconia, a silica-magnesia, a silica-alumina-titania, and a silica-alumina-zirconia or two sorts or more, or a multiple oxide consists of one sort chosen from a silica alumina, a silica-titania, a silica-zirconia, a silica-magnesia, a silica-alumina-titania, and a silica-alumina-zirconia or two sorts or more, and a USY zeolite.

[0010]

Moreover, a binder part consists of one sort chosen from an alumina and a boria-alumina, or two sorts or more, it is desirable that a metal component is one sort in molybdenum, a tungsten, cobalt, a rhodium, iridium, nickel, palladium, and platinum or two sorts or more, and it is still more desirable about the particle of a multiple oxide that that the diameter of whose is 10 micrometers or less is at least 60%.

[0011]

The process which mixes the multiple oxide fine particles in which the manufacture approach of the hydrocracking catalyst by this invention contains fine particles with a diameter of 10 micrometers or less at least 60%, and a binder component, The process which dries and calcinates mixture and forms support, and the process which supports at least one sort of metal components chosen as the support from the 6th group, the 9th group, and the 10th group of the periodic table are included. By that cause (A) A central pore diameter is 40-100A, and the pore volume of the range which is the pore diameter of 40-100A is 0.1 mL/g at least. And the pore volume of the range of 0.05-0.5-micrometer (B) pore diameter is 0.05 - 0.5 mL/g, and the pore volume which is the pore diameter of 0.5-10 micrometers is the approach of acquiring the hydrocracking catalyst which is less than 0.05 mL/g.

[0012]

In the above-mentioned approach, it is desirable that a binder component consists of one sort chosen

from aluminum hydration oxide and the aluminum hydration oxide containing boria or two sorts or more.

[0013]

The hydrocracking approach of a hydrocarbon oil of following this invention is an approach convertible into the product which decreased the fraction which is contained in the hydrocarbon oil in a hydrocarbon oil, and which has the high boiling point relatively by contacting a hydrocarbon oil for the hydrocracking catalyst of above-mentioned this invention under existence of hydrogen.

[0014]

Explanation of the desirable example for inventing Hereafter, it divides into the manufacture approach of the pore property of a catalyst, the component of a catalyst, and a catalyst, a hydrocracking reaction, etc., and the hydrocracking catalyst of this invention and the detail of the hydrocracking approach are explained.

[0015]

[Pore property of a hydrocracking catalyst] The hydrocracking catalyst concerning this invention is characterized by satisfying the pore property of fulfilling both the conditions of following (A) and (B).

(A) A central pore diameter is 40-100A, and the pore volume of the range which is the pore diameter of 40-100A should be 0.1 mL/g at least.

(B) The pore volume of the range of 0.05-0.5-micrometer pore diameter is 0.05 - 0.5 mL/g, and the pore volume of the pore volume which is the pore diameter of 0.5-10 micrometers should be less than 0.05 mL/g.

[0016]

the so-called pore property of meso pore, i.e., the pore property about the conditions of the above (A), is measured with a nitrogen gas absorption method -- having -- BJH -- the relation between pore volume and a pore diameter is computable with law etc. Moreover, a central pore diameter says the pore diameter from which the accumulation pore volume from a side with a large pore diameter becomes V/2, when setting to V pore volume obtained on condition that phase counter pressure 0.9667 in a nitrogen gas absorption method. What has the central pore diameter of a hydrocracking catalyst in the range of 40-100A, and is in the range whose central pore diameter is 45-90A further, and the thing which is in the range whose central pore diameter is 50-85A especially are used preferably. The pore volume of the range of 40-100A pore diameter is 0.1 mL/g at least, and, as for especially this pore volume, it is desirable that it is 0.15 - 0.6 mL/g 0.1 to 1.0 mL/g.

[0017]

Fundamentally, the pore property of the above-mentioned meso pore of ************ can be acquired by controlling the pore property of a multiple oxide to have the pore property of the above-mentioned meso pore. This is because the pore property of the meso pore of a multiple oxide is usually maintained until a catalyst is formed with a multiple oxide.

[0018]

The so-called pore property of macro pore, i.e., the pore property about the conditions of the above (B), can be measured using a method of mercury penetration, the contact angle of mercury is made into 140 degrees, surface tension is made into 480 dynes/cm, and all pores are computable, assuming that it is a cylindrical shape. The hydrocracking catalyst 0.05 - 0.5 mL/g and whose pore volume with a diameter of 1 micrometers or more pore volume with a diameter of 0.05-1 micrometer is less than 0.05 mL/g is used. Furthermore, pore volume with a diameter of 0.05-0.5 micrometers is 0.05 - 0.5 mL/g especially 0.04 to 0.5 mL/g, and it is desirable in order that it may raise the mechanical strength of a catalyst that less than 0.05 mL/g of less than 0.02 more mL/g of pore volume with a diameter of 1 micrometers or more is 0.01 mL/g especially.

[0019]

The pore property of macro pore is controllable by the filling factor with the binder of the opening between multiple oxide particles, and an opening. The opening between multiple oxide particles is controllable by the particle size of a multiple oxide particle. The above-mentioned filling factor is controllable by the mixing ratio or weight ratio of the binder and multiple oxide particle which are

mentioned later.
[0020]
The pore property of meso pore and macro pore may be influenced again according to the description and the kneading conditions of a binder which are mentioned later.
[0021]
[Multiple oxide] The multiple oxide as used in the field of this invention is a multiple oxide which has solid acid nature. for example, duality -- although K.Shibata, T.Kiyoura, J.Kitagawa, K.Tanabe, Bull.Chem.Soc.Jpn., 46, and the thing by which the acid manifestation is checked by 2985 (1973) are begun and many things are known for the multiple oxide, a silica alumina, a silica-titania, a silica-zirconia, and a silica-magnesia are used preferably. As a multiple oxide, a silica-alumina-titania and the silica-alumina-zirconia of 3 yuan are used preferably. Moreover, zeolites, such as a USY zeolite, are contained in the multiple oxide as used in the field of this invention, and it can use for it.
[0022]
A USY zeolite is a super-stability Y mold zeolite, it has high drag force in crystalline degradation by acid treatment, high temperature processing, steam treatment, etc., and the content of alkali-metal ion is Y mold zeolite which is less than 1 % of the weight preferably, and is characterized less than 4% of the weight by the lattice constant of less than 24.50A and 5, or the silica (SiO2) / alumina (aluminum 2O3) mole ratio beyond it.
[0023]
If the thing in the range whose central pore diameter the volume of the pore in the range of 40-100A pore diameter is 0.1 mL/g at least, and is 35-100A is used when using the thing of the gestalt of fine particles as a raw material of hydrocracking catalyst manufacture about multiple oxides other than a USY zeolite, it will be easy to acquire the pore property of the hydrocracking catalyst of this invention, and will be used preferably. Furthermore, the thing in the range whose central pore diameter is 40-90A, and the thing which is in the range whose central pore diameter is 45-85A especially are used preferably. Moreover, if the above pore properties are fulfilled, multiple oxide fine particles with a more big specific surface area will be used preferably. That whose specific surface area is more than 250m2/g is especially desirable still more desirable, and, specifically, the thing more than 350m2/g is used suitably more than 300m2/g.
[0024]
If that whose diameter of floc is 10 micrometers or less uses the multiple oxide which is at least 60% about the multiple oxide as used in the field of this invention in using the thing of the gestalt of fine particles, since it will be easy to acquire the macro pore property of this invention and will be easy to acquire the catalyst which has sufficient mechanical strength, it is desirable. A certain thing has [that that whose diameter of floc is 10 micrometers or less should just be at least 60%] that especially desirable about the whole when using the fine particles of two or more sorts of multiple oxides whose diameter is 1-10 micrometers 70% or more 60% or more. The particle size of floc irradiates laser light at the particle group distributed underwater, and can be measured by asking from the scattered light etc. Moreover, it may pretreat and multiple oxide fine particles may be used so that that whose diameter of floc is 10 micrometers or less may become at least 60% with dry grinding or wet grinding. In the catalyst manufactured using the floc of a multiple oxide, the multiple oxide exists as a particle of the almost same magnitude as the magnitude of floc.
[0025]
[Binder part] As for the binder part used by this invention, it is desirable to consist of one sort chosen from an alumina and a boria-alumina or two sorts or more. Aluminas here are aluminum oxide, a hydroxide, and/or hydration oxide, and a boria-alumina is the aluminum oxide, the hydroxide, and/or hydration oxide containing boria. Boria may be contained as mixture and may be contained as the solid solution or a conjugated compound.
[0026]
the fine particles (only henceforth alumina fine particles) which the binder component used as the raw material of support becomes from an aluminum hydroxide and/or hydration oxide -- since using the

aluminum hydration oxide which has boehmite structures, such as pseudo-boehmite, especially can improve hydrocracking activity and middle-cut selectivity, it is desirable. moreover, the fine particles (only henceforth boria-alumina fine particles) which a binder component becomes from the aluminum hydroxide and/or hydration oxide containing boria -- since using the aluminum hydration oxide which has boehmite structures, such as pseudo-boehmite which contains boria especially, can improve hydrocracking activity and middle-cut selectivity, it is desirable.

[0027]

As for especially the weight of a binder part, it is desirable to consider as 15 - 35 % of the weight five to 50% of the weight among the sum total weight of the multiple oxide part which constitutes a catalyst, and a binder part. Under in this range, the mechanical strength of a catalyst tends to fall, and if this range is exceeded, hydrocracking activity and middle-cut selectivity will fall relatively. When using a USY zeolite as a multiple oxide, as for especially the weight of a USY zeolite part, it is desirable to consider as 0.2 - 20 % of the weight 0.1 to 30% of the weight among the sum total weight of the multiple oxide part which constitutes a catalyst, and a binder part. Under in this range, it is hard to discover the improvement effectiveness in decomposition activity by having used the USY zeolite, and if this range is exceeded, middle-cut selectivity will fall relatively. When using silica alumina as a multiple oxide, it uses among silica alumina so that an alumina may be set to 1-20 by the mole ratio of 10 - 60 % of the weight, or a silica/alumina.

[0028]

[Metal component]

One sort or two sorts or more of metal components chosen from the 6th group, the 9th group, and the 10th group are included in the hydrocracking catalyst of this invention. As a metal chosen from the 6th group used for the catalyst of this invention, the 9th group, and the 10th group, molybdenum, a tungsten, cobalt, a rhodium, iridium, nickel, platinum, and palladium are used especially suitably. What mixed two or more sorts at least one sort is sufficient as these metals. As for the addition of these metals, it is desirable that the total quantity of the 6th group who occupies in a hydrocracking catalyst, the 9th group, and the 10th group element adds so that it may become 0.1 - 30 % of the weight especially 0.05 to 35% of the weight. When using molybdenum as a metal, as for the addition, it is desirable to consider as 5 - 20 % of the weight among a hydrocracking catalyst. When using a tungsten as a metal, as for the addition, it is desirable to consider as 5 - 30 % of the weight among a hydrocracking catalyst. About the addition of molybdenum or a tungsten, if fewer than the above-mentioned range, the hydrogenation functions of an active metal required for a hydrocracking reaction run short, and it is not desirable. On the contrary, if [than the above-mentioned range] more, condensation of the added active metal component is easy to happen and is not desirable. In using molybdenum or a tungsten as a metal, when it adds cobalt or nickel, the hydrogenation function of an active metal improves and it is much more desirable. As for the cobalt in that case, or the sum total addition of nickel, it is desirable to consider as 0.5 - 10 % of the weight among a hydrocracking catalyst. When using one sort in a rhodium, iridium, platinum, and palladium, or two sorts or more as a metal, as for the addition, it is desirable to consider as 0.1 - 5 % of the weight. In under this range, if sufficient hydrogenation function is not obtained but this range is exceeded, since it is not economical, it is not desirable.

[0029]

[A presentation of a hydrocracking catalyst]

In the hydrocracking catalyst of this invention The metallic element of the 6th group, the 9th group, and the 10th group, About the presentation of the element except boron, carbon, hydrogen, nitrogen, and oxygen The ratio of the sum total of the number of mols of oxide conversion (for example, mol as SiO2, TiO2, ZrO2, and MgO number) of elements other than aluminum and the number of mols of oxide conversion of aluminum (mol as aluminum 2O3 number) It is still more desirable the range of 0.5-10 and that it is in the range of 0.7-7. When exceeding under this range and this range, the mechanical strength of hydrocracking activity, middle-cut selectivity, or a catalyst falls and is not desirable.

[0030]

[The manufacture approach of a hydrocracking catalyst]

Other approaches can also be used for it, if the catalyst which has a predetermined pore property is producible although it is producible by drying and calcinating after it dries, calcinating it, creating support, after such a fabricated catalyst kneads and fabricates multiple oxide fine particles and a binder component, and carrying out sinking-in support of the metal component further.

[0031]

The kneading machine generally used for catalyst preparation can be used for kneading. Usually, although an approach which throws in a raw material, adds water and is mixed with an impeller is used suitably, especially limitation does not have the order of materials charging of a raw material and an additive etc. Although the indifferent water is added in the case of kneading, especially when a raw material is a slurry-like, it is not necessary to add water. Moreover, as a liquid to add, organic solvents, such as ethanol, isopropanol, an acetone, a methyl ethyl ketone, and methyl isobutyl ketone, are sufficient. Although the temperature and mixing time at the time of kneading change with the multiple oxides and binder components used as a raw material, if it is the conditions from which desirable pore structure is acquired, there will be especially no limit. Similarly, as long as it is within the limits by which the description of the catalyst of this invention is maintained, organic compounds, such as bases, such as acids, such as a nitric acid, and ammonia, a citric acid, and ethylene glycol, a water soluble polymer compound like cellulose ether and polyvinyl alcohol, ceramic fiber, etc. may be added and kneaded.

[0032]

Shaping after kneading can use the shaping approach generally used for catalyst preparation. Extrusion molding using a screw-type extruder etc. and shaping by the oil dropping method which can be fabricated efficiently spherically which can be especially fabricated efficiently in the configuration of arbitration, such as a pellet type, are used preferably. Although there is especially no limit in the size of a moldings, if it is a cylinder-like pellet, for example, a thing with a diameter [of 0.5-20mm] and a die length of about 0.5-15mm can usually be obtained easily.

[0033]

Let the moldings obtained as mentioned above be support by carrying out desiccation and baking processing. As for this baking processing, it is desirable to calcinate at the temperature of 300 degrees C - 900 degrees C in gas ambient atmospheres, such as air or nitrogen, for 0.1 to 20 hours.

[0034]

Although there is especially no limit in the approach of supporting a metal component to support, the sinking-in method by the spray, immersion, etc., an ion-exchange method, etc. are used suitably. Moreover, more metal components can be supported by repeating support processing and desiccation processing. The hydrocracking catalyst which made support support a metal component is desirable in order that calcinating at the temperature of 300 degrees C - 900 degrees C in gas ambient atmospheres, such as air or nitrogen, for 0.1 to 20 hours may raise the activity of a catalyst.

[0035]

[The mechanical strength of a hydrocracking catalyst and support]

As for the mechanical strength of a hydrocracking catalyst, 4kg or more 3kg or more is more preferably obtained as side-face collapse reinforcement of a cylinder pellet with a diameter of 1.6mm. Moreover, although it is desirable to have mechanical strength sufficient also about shaping support in order to manufacture a catalyst with the sufficient yield when carrying out sinking-in support of the metal component and creating a catalyst after creating shaping support, as for the mechanical strength of the shaping support in this invention, 4kg or more 3kg or more is more preferably obtained as side-face collapse reinforcement of a cylinder pellet with a diameter of 1.6mm.

[0036]

The [hydrocracking reaction approach] The hydrocracking approach of the hydrocarbon oil by this invention is the approach of performing by facing changing into the product which decreased the fraction which has the fraction which is contained in the hydrocarbon oil in the hydrocarbon oil of a raw material, and which has the high boiling point relatively, or the boiling point higher than specific temperature, and contacting a hydrocarbon oil for the above catalysts under existence of hydrogen.

[0037]
Although there is especially no limit in the hydrocarbon oil which can be used as a raw material, what contains the fraction which has the boiling point 250 degrees C or more 80% of the weight or more is used preferably. Although there is especially no limit also in the origin of the hydrocarbon oil which can be used as a raw material, a thing, a Fischer-Tropsch-synthesis oil, etc. which are guided from a crude oil, coal liquid, an oil shale, an oil sand, etc. are used preferably. Although the hydrocarbon oil used as a raw material contains impurities other than a hydrocarbon, the way with few impurity contents is desirable, and what pretreated hydrorefining, deasphaltings, etc., such as desulfurization, denitrification, and demetallization, is used preferably. The ingredient with which the metal matter does not carry out deposition to meso pore and macro pore, but an early pole diameter can be maintained especially by that cause is desirable. concrete -- any for a part for vanadium, and nickel -- although -- 0.0001% of the weight of stock oil is much more preferably desirable 0.0002 weight preferably 0.0005 or less % of the weight.
[0038]
In the hydrocracking approach of the hydrocarbon oil by this invention, although changed into the product which decreased the fraction which has the boiling point higher than specific temperature for the hydrocarbon oil of a raw material, it is desirable to be able to choose the temperature of arbitration as specific temperature here according to the desired specified substance, and to choose 180-degree-C or more temperature of 400 degrees C or less as it. Moreover, as for the hydrocarbon oil used as a raw material, it is desirable to contain the fraction which has the boiling point beyond the specific temperature chosen here 50% of the weight or more, and it is desirable to contain 90% of the weight or more especially further 80% of the weight or more.
[0039]
In the hydrocracking approach of the hydrocarbon oil by this invention, after filling up a reactor, a catalyst pretreats desiccation, reduction, sulfuration, etc. and may be used. Especially when the 6th group's element is included as a metal component, before using it for a hydrocracking reaction, being applied to sulfidization is desirable.
[0040]
In the hydrocracking approach of the hydrocarbon oil by this invention, although a hydrocracking reaction is performed under existence of hydrogen, it is desirable to carry out under pressurization conditions [as / whose total pressure is 2 or more-MPa 30 or less MPa]. The liquid space velocity (LHSV) suitable for the hydrocracking approach of the hydrocarbon oil by this invention is one or less [1 or more / 0.2h - / h / 5.0 / -], and one or less [1 or more / 0.3h - / h / 3.0 / -] is especially desirable. The hydrogen / stock oil delivery late suitable for the hydrocracking approach of the hydrocarbon oil by this invention are below 100 or more NL/L5000NL/L. In the hydrocracking approach of the hydrocarbon oil by this invention, it is desirable to react at 250-degree-C or more temperature of 500 degrees C or less, and it is desirable to carry out below 300 degrees C or more especially 450 degrees C.
[0041]
Example Hereafter, an example and the example of a comparison are used for the catalyst and its manufacture approach list of this invention, and the hydrocracking approach is explained to them in detail and concretely.
[Catalyst A] As it is the following, they are W 11.0 % of the weight, 1.0 % of the weight of nickel, and a silica alumina. 67.9 % of the weight, alumina The catalyst A which consists of 17.0 % of the weight was prepared.
[0042]
Kneading mixing of 1136g (a silica / alumina mole ratio 7.4, 93.4 % of the weight of things with a condensation particle size of 1-10 micrometers, 16.4 % of the weight of loss on ignition) of silica-alumina fine particles and the 325g (27.0 % of the weight of loss on ignition) of the pseudo-boehmite fine particles was carried out, and it extruded from circular opening with a diameter of 1.6mm, and fabricated in the shape of a cylindrical shape. This moldings was dried at 130 degrees C for 15 hours, and, subsequently the support of a silica alumina / alumina mixed stock was prepared by calcinating at

600 degrees C under the air current of air for 1 hour. The average side-face collapse reinforcement of this support was 6.3kg.
[0043]
After carrying out spray sinking in of the ammonium metatungstate water solution and drying at 130 degrees C to this support for 15 hours, it carried out spray sinking in of the nickel nitrate water solution, and dried at 130 degrees C for 15 hours. Subsequently, it calcinated at 500 degrees C under the air current of air for 30 minutes. In this way, Catalyst A was acquired.
[0044]
When the pore property of this catalyst A was measured with the nitrogen gas absorption method, the volume of the pore in the range of 40-100A pore diameter was 0.328 mL/g, and the central pore diameter was 51A. Moreover, as a result of measuring the pore property of Catalyst A with a method of mercury penetration, the pore volume whose volume of the pore in the range of 0.05-0.5-micrometer pore diameter is 0.085 mL/g and the pore diameter of 0.5 micrometers - 10 micrometers was 0.001 mL/g. In addition, the volume of the pore in the range of 0.05-1-micrometer pore diameter is 0.086 mL/g, and it also turned out that the volume of the pore in the range of 1-10-micrometer pore diameter is less than 0.001 mL/g.
[0045]
Rhine A showed the pore property of Catalyst A among drawing 1 . While the sharp peak has appeared in the range of 40-100A pore diameter (meso pore), it turns out that the peak remarkable also in the range of 0.05-0.5-micrometer pore diameter (macro pore) has appeared.
[0046]
Moreover, the average side-face collapse reinforcement of this catalyst A was 5.9kg.
[0047]
As it is below the [catalyst B], they are W 16.5 % of the weight, 1.5 % of the weight of nickel, and a silica alumina. 61.1 % of the weight, USY zeolite 0.8 % of the weight, alumina The catalyst B which consists of 15.5 % of the weight was prepared.
[0048]
Kneading mixing of 1372g [of silica-alumina fine particles] (silica / alumina mole ratio 4.4, 94.4 % of the weight [of things with a condensation particle size of 1-10 micrometers], 16.9 % of the weight of loss on ignition) and USY zeolite 16.1g (a silica / alumina mole ratio 67.9 % of the weight of things with 30.3, Na content of 0.02 % of the weight, a lattice constant [of 24.29A], and a condensation particle size of 1-10 micrometers, 10.6 % of the weight of loss on ignition) and the 395g (27.0 % of the weight of loss on ignition) of the pseudo-boehmite fine particles be carried out, and it extruded from circular opening with a diameter of 1.6mm, and fabricated in the shape of a cylindrical shape. This moldings was dried at 130 degrees C for 15 hours, and, subsequently the support of a silica alumina / USY zeolite / alumina mixed stock was prepared by calcinating at 600 degrees C under the air current of air for 1 hour. The average side-face collapse reinforcement of this support was 4.0kg.
[0049]
After carrying out spray sinking in of the ammonium metatungstate water solution and drying at 130 degrees C to this support for 15 hours, it carried out spray sinking in of the nickel nitrate water solution, and dried at 130 degrees C for 15 hours. Subsequently, it calcinated at 500 degrees C under the air current of air for 30 minutes. In this way, Catalyst B was acquired.
[0050]
When the pore property of this catalyst B was measured with the nitrogen gas absorption method, the volume of the pore in the range of 40-100A pore diameter was 0.279 mL/g, and the central pore diameter was 52A. Moreover, the volume of the pore which is in the range whose volume of the pore in the range of 0.05-0.5-micrometer pore diameter is 0.101 mL/g and the pore diameter of 0.5-10 micrometers as a result of measuring the pore property of Catalyst B with a method of mercury penetration was 0.004 mL/g. In addition, the volume of the pore in the range of 0.05-1-micrometer pore diameter is 0.104 mL/g, and it also turned out that the volume of the pore in the range of 1-10-micrometer pore diameter is 0.001 mL/g.

[0051]
Rhine B showed the pore property of Catalyst B among drawing 1 . Like Catalyst A, while the sharp peak has appeared in the range of 40-100A pore diameter (meso pore), it turns out that the peak remarkable also in the range of 0.05-0.5-micrometer pore diameter (macro pore) has appeared.
[0052]
The average side-face collapse reinforcement of Catalyst B was 4.4kg.
[0053]
[Catalyst C] As it is the following, they are W 22.0 % of the weight, 2.0 % of the weight of nickel, and a silica alumina. 50.9 % of the weight, USY zeolite 4.9 % of the weight, boria-alumina The catalyst C which consists of 13.9 % of the weight was prepared.
[0054]
1136g (a silica / alumina mole ratio 93.4 % of the weight of things with a 7.4 and a condensation particle size of 1-10 micrometers) of silica-alumina fine particles 16.4 % of the weight [of loss on ignition], and USY zeolite 102g (a silica / alumina mole ratio 30.3 and 0.02 % of the weight of Na contents) 67.9 % of the weight of things with a lattice constant [of 24.29A], and a condensation particle size of 1-10 micrometers, Kneading mixing of 10.6 % of the weight of loss on ignition and the 324g (2.6 % of the weight of boron contents, 19.7 % of the weight of loss on ignition) of the boria-alumina fine particles was carried out, and it extruded from circular opening with a diameter of 1.6mm, and fabricated in the shape of a cylindrical shape. This moldings was dried at 130 degrees C for 15 hours, and, subsequently the support of a silica alumina / USY zeolite / boria-alumina mixed stock was prepared by calcinating at 600 degrees C under the air current of air for 1 hour. The average side-face collapse reinforcement of this support was 6.6kg.
[0055]
After carrying out spray sinking in of the ammonium metatungstate water solution and drying at 130 degrees C to this support for 15 hours, it carried out spray sinking in of the nickel nitrate water solution, and dried at 130 degrees C for 15 hours. Subsequently, it calcinated at 500 degrees C under the air current of air for 30 minutes. In this way, Catalyst C was acquired.
[0056]
When the pore property of this catalyst C was measured with the nitrogen gas absorption method, the volume of the pore in the range of 40-100A pore diameter was 0.194 mL/g, and the central pore diameter was 69A. Moreover, as a result of measuring the pore property of Catalyst C with a method of mercury penetration, the volume of the pore in the range of 0.05-0.5-micrometer pore diameter was 0.076 mL/g, and the volume of the pore which is the pore diameter of 0.5-10 micrometers was 0.001 mL/g. The average side-face collapse reinforcement of this catalyst C was 8.4kg.
[0057]
[Catalyst D] As it is the following, they are W 22.0 % of the weight, 2.0 % of the weight of nickel, and a silica alumina. 53.3 % of the weight, USY zeolite 2.4 % of the weight, alumina The catalyst D which consists of 13.9 % of the weight was prepared.
[0058]
Kneading mixing of 1143g [of silica-alumina fine particles] (silica / alumina mole ratio 4.4, 94.4 % of the weight [of things with a condensation particle size of 1-10 micrometers], 16.9 % of the weight of loss on ignition) and USY zeolite 49g (a silica / alumina mole ratio 67.9 % of the weight of things with 30.3, Na content of 0.02 % of the weight, a lattice constant [of 24.29A], and a condensation particle size of 1-10 micrometers, 10.6 % of the weight of loss on ignition) and the 340g (27.0 % of the weight of loss on ignition) of the pseudo-boehmite fine particles be carried out, and it extruded from circular opening with a diameter of 1.6mm, and fabricated in the shape of a cylindrical shape. This moldings was dried at 130 degrees C for 15 hours, and, subsequently the support of a silica alumina / USY zeolite / alumina mixed stock was prepared by calcinating at 600 degrees C under the air current of air for 1 hour. The average side-face collapse reinforcement of this support was 4.0kg.
[0059]
After carrying out spray sinking in of the ammonium metatungstate water solution and drying at 130

degrees C to this support for 15 hours, it carried out spray sinking in of the nickel nitrate water solution, and dried at 130 degrees C for 15 hours. Subsequently, it calcinated at 500 degrees C under the air current of air for 30 minutes. In this way, Catalyst D was acquired.

[0060]

When the pore property of this catalyst D was measured with the nitrogen gas absorption method, the volume of the pore in the range of 40-100A pore diameter was 0.231 mL/g, and the central pore diameter was 52A. Moreover, as a result of measuring the pore property of this catalyst D with a method of mercury penetration, the volume of the pore in the range of 0.05-0.5-micrometer pore diameter was [pore volume with a 0.070 mL/g and a pore diameter of 0.5-10 micrometers or more] 0.003 mL/g. In addition, the volume of the pore in the range of 0.05-1-micrometer pore diameter was 0.072 mL/g, and the volume of the pore in the range which is the pore diameter of 1-10 micrometers was 0.001 mL/g.

[0061]

The average side-face collapse reinforcement of this catalyst D was 4.7kg.

[0062]

[The hydrocracking reaction using Catalyst A and Catalyst B]

The evaluation approach 1: The fixed-bed circulation type reactor of catalyst fill 100mL is filled up with Catalyst A. 15-degree C consistency 0.831 g/mL, 262.9 degrees C of initial boiling points after carrying out preliminary sulfuration, The fraction of 293 degrees C or more of boiling points 97.8 % of the weight, less than 0.001 % of the weight of total sulfur concentration, Less than 0.0001 % of the weight of total nitrogen concentration, less than 0.0001 % of the weight of vanadium concentration, The vacuum gas oil which is less than 0.0001 weight of nickel concentration is used. Pressure 15MPa, A hydrocracking reaction is performed by hydrogen / stock oil delivery-late 800 NL/L, LHSV=1.36h-1, reaction temperature 390 and 380, and the 370 or 360-degree C reaction condition. When asked for the middle-cut yield of the boiling range of 127-293 degrees C of boiling points in the reaction temperature which takes the fraction of 293 degrees C or more of boiling points to convert with 60% of the weight of an invert ratio, and its invert ratio, they were 376.4 degrees C and 39.9 % of the weight, respectively.

[0063]

When asked for the middle-cut yield of the boiling range of 127-293 degrees C of boiling points in the reaction temperature taken to fill up the same reactor with Catalyst B, to perform a hydrocracking reaction on the same conditions as the above, and to convert the fraction of 293 degrees C or more of boiling points with 60% of the weight of an invert ratio, and its invert ratio, they were 367.7 degrees C and 40.3 % of the weight, respectively.

[0064]

The evaluation approach 2: The following evaluations were performed again on conditions which are different from the above about Catalyst A. When the above-mentioned fixed-bed circulation type reactor was filled up with Catalyst A, and the hydrocracking reaction was performed using the same vacuum gas oil as the above by pressure 15MPa, hydrogen / stock oil delivery-late 800 NL/L, LHSV=1.36h-1, and the reaction condition with a reaction temperature of 380 degrees C and having been asked for the invert ratio of the fraction of 293 degrees C or more of boiling points, and the middle-cut yield of the boiling range of 127-293 degrees C of boiling points, it turned out that they are 64.5 % of the weight and 64.4 % of the weight, respectively.

[0065]

When the above-mentioned fixed-bed circulation type reactor was filled up with Catalyst B, and the hydrocracking reaction was performed using the same vacuum gas oil as the above by pressure 15MPa, hydrogen / stock oil delivery-late 800 NL/L, LHSV=1.36/h-1, and the reaction condition with a reaction temperature of 380 degrees C and having been asked for the invert ratio of the fraction of 293 degrees C or more of boiling points, and the middle-cut yield of the boiling range of 127-293 degrees C of boiling points, it turned out that they are 79.2 % of the weight and 48.9 % of the weight, respectively.

[0066]

[The hydrocracking reaction using Catalyst C and Catalyst D]

The evaluation approach 1: The fixed-bed circulation type reactor of catalyst fill 100mL is filled up with

Catalyst C. 15-degree C consistency 0.9060 g/mL, 309.3 degrees C of initial boiling points after carrying out preliminary sulfuration, 91.3 % of the weight of fractions of 360 degrees C or more of boiling points, 0.46 % of the weight of total sulfur concentration, 0.081 % of the weight of total nitrogen concentration, less than 0.0001 % of the weight of vanadium concentration, The vacuum gas oil which is less than 0.0001 % of the weight of nickel concentration is used. Pressure 15MPa, A hydrocracking reaction is performed by hydrogen / stock oil delivery-late 1000 NL/L, LHSV=1.36h-1, and the reaction condition with a reaction temperature of 420,410,400 degrees C. when asked for the middle-cut yield of the boiling range of 127-360 degrees C of boiling points in the reaction temperature which takes the fraction of 360 degrees C or more of boiling points to convert with 60% of the weight of an invert ratio, and its invert ratio, 410.0 degrees C came out 41.2% of the weight, respectively.
[0067]
When asked for the middle-cut yield of the boiling range of 127-360 degrees C of boiling points in the reaction temperature taken to fill up the same reactor with Catalyst D, to perform a hydrocracking reaction on the same conditions as the above, and to convert the fraction of 360 degrees C or more of boiling points with 60% of the weight of an invert ratio, and its invert ratio, they were 411.9 degrees C and 45.6 % of the weight, respectively.
[0068]
The evaluation approach 2: The following evaluation trials were performed again on conditions which are different from the above-mentioned evaluation conditions about Catalysts C and D.
[0069]
When the above-mentioned fixed-bed circulation type reactor was filled up with Catalyst C, and the hydrocracking reaction was performed using the same vacuum gas oil as the above by pressure 15MPa, hydrogen / stock oil delivery-late 1000 NL/L, LHSV=1.36h-1, and the reaction condition with a reaction temperature of 400 degrees C and having been asked for the invert ratio of the fraction of 360 degrees C or more of boiling points, and the middle-cut yield of the boiling range of 127-360 degrees C of boiling points, it turned out that they are 40.9 % of the weight and 72.4 % of the weight, respectively.
[0070]
Moreover, when the above-mentioned fixed-bed circulation type reactor was filled up with Catalyst D, and the hydrocracking reaction was performed using the same vacuum gas oil as the above by pressure 15MPa, hydrogen / stock oil delivery-late 1000 NL/L, LHSV=1.36h-1, and the reaction condition with a reaction temperature of 400 degrees C and having been asked for the invert ratio of the fraction of 360 degrees C or more of boiling points, and the middle-cut yield of the boiling range of 127-360 degrees C of boiling points, it turned out that they are 39.4 % of the weight and 81.3 % of the weight, respectively.
[0071]
Example of a comparison [Catalyst E] As it is the following, they are W 11.0 % of the weight, 1.0 % of the weight of nickel, and a silica alumina. 67.9 % of the weight, alumina The catalyst E which consists of 17.0 % of the weight was prepared.
[0072]
Kneading mixing of 1137g (a silica / alumina mole ratio 4.1, 34.4 % of the weight of things with a condensation particle size of 1-10 micrometers, 23.9 % of the weight of loss on ignition) of silica-alumina fine particles and the 296g (27.0 % of the weight of loss on ignition) of the pseudo-boehmite fine particles was carried out, and it extruded from circular opening with a diameter of 1.6mm, and fabricated in the shape of a cylindrical shape. This moldings was dried at 130 degrees C for 15 hours, and, subsequently the support of a silica alumina / alumina mixed stock was prepared by calcinating at 600 degrees C under the air current of air for 1 hour. The average side-face collapse reinforcement of this support was 2.1kg. After carrying out spray sinking in of the ammonium metatungstate water solution and drying at 130 degrees C to this support for 15 hours, it carried out spray sinking in of the nickel nitrate water solution, and dried at 130 degrees C for 15 hours. Subsequently, it calcinated at 500 degrees C under the air current of air for 30 minutes. In this way, Catalyst E was acquired.
[0073]
When the pore property of this catalyst E was measured with the nitrogen gas absorption method, the

volume of the pore in the range of 40-100A pore diameter was 0.442 mL/g, and the central pore diameter was 62A. Moreover, as a result of measuring the pore property of this catalyst E with a method of mercury penetration, the volume of the pore in the range of 0.05-0.5-micrometer pore diameter was 0.026 mL/g, and pore volume with a pore diameter of 0.5-10 micrometers or more was 0.105 mL/g. In addition, the volume of the pore in the range of 0.05-1-micrometer pore diameter was 0.053 mL/g, and the volume of the pore in the range which is the pore diameter of 1-10 micrometers was 0.078 mL/g.
[0074]
Rhine E showed the pore property of Catalyst E among drawing 1 . The sharp peak has appeared like Catalyst A in the range of 40-100A pore diameter (meso pore). However, it differed in Catalysts A and B, and the peak of macro pore has appeared in the field exceeding the pore diameter of 1 micrometer.
[0075]
The average side-face collapse reinforcement of this catalyst E was 3.2kg.
[0076]
[The hydrocracking reaction using Catalyst E]
The evaluation approach 1: When asked for the reaction temperature taken to fill up the fixed-bed circulation type reactor of catalyst fill 100mL with Catalyst E, to perform a hydrocracking reaction on the same conditions as the evaluation approach 1 which followed Catalyst A and Catalyst B, and to convert the fraction of 293 degrees C or more of boiling points with 60% of the weight of an invert ratio, and the middle-cut yield of the boiling range of 127-293 degrees C of boiling points in the invert ratio, they were 378.8 degrees C and 37.0 % of the weight, respectively.
[0077]
The evaluation approach 2: When the fixed-bed circulation type reactor of catalyst fill 100mL was filled up with Catalyst E, and the hydrocracking reaction was performed on condition that [same] the evaluation approach 2 which followed Catalyst A and having been asked for the invert ratio of the fraction of 293 degrees C or more of boiling points, and the middle-cut yield of the boiling range of 127-293 degrees C of boiling points, they were 59.6 % of the weight and 61.0 % of the weight, respectively.
[0078]
The measuring device and approach which were used in the above-mentioned example and the example of a comparison are indicated below.
[0079]
[Particle-size-distribution measuring method of floc] It measured by the wet measuring method using the Nikkiso Co., Ltd. MICROTRAC grading-analysis meter. This makes fine particles distribute underwater, irradiates laser light at the flowing floc group, and performs grading analysis by the forward-scattering light.
[0080]
[Measuring method of a pore property] The AutoPore9200 mold measuring instrument made from Micromeritics was used for measurement of the pore property by the method of mercury penetration. The ASAP2400 mold measuring instrument made from Micromeritics was used for measurement of the pore property by the nitrogen gas absorption method.
[0081]
[Measuring method of average side-face collapse reinforcement] Using the TH-203CP tablet disruptive strength measuring instrument made from Toyama Industry, extrusion molding was carried out to the shape of a cylinder, and side-face collapse reinforcement was measured using the sample dried and calcinated. The measurement probe used the thing of the circle configuration whose tip is the diameter of 5mm. The actuation which applies a measurement sample in the center of a side face of a cylinder sample, and measures it was repeated 20 times, and the average was computed.
[0082]
[A definition of an invert ratio and middle-cut yield]
The invert ratio and middle-cut selectivity which show the activity of the catalyst in an example and the example of a comparison were defined as follows.
[0083]

Invert ratio =[1-(weight [of the fraction of 293 degrees C or more of boiling points occupied in weight % / stock oil of the fraction of 293 degrees C or more of boiling points occupied in a generation oil] %)] x100 of the fraction of 293 degrees C or more of boiling points (% of the weight)
Invert ratio =[1-(weight [of the fraction of 360 degrees C or more of boiling points occupied in weight % / stock oil of the fraction of 360 degrees C or more of boiling points occupied in a generation oil] %)] x100 of the fraction of 360 degrees C or more of boiling points (% of the weight)
Middle-cut yield =[(weight of fraction of boiling range of 127-293 degrees C of boiling points in product)/(weight of product except hydrogen-sulfide and ammonia)] x100 of the boiling range of 127-293 degrees C of boiling points (% of the weight)
Middle-cut yield =[(weight of fraction of boiling range of 127-360 degrees C of boiling points in product)/(weight of product except hydrogen-sulfide and ammonia)] x100 of the boiling range of 127-360 degrees C of boiling points (% of the weight)
[0084]
[The index of decomposition activity and middle-cut selectivity]
The middle-cut yield of the boiling range of 127-293 degrees C of boiling points in the reaction temperature which an example and the example of a comparison take the fraction of 293 degrees C or more of boiling points shown as an index of the decomposition activity of a catalyst and middle-cut selectivity converting with 60% of the weight of an invert ratio, and its invert ratio is the following, and was made and computed.
[0085]
About the reaction which converts the fraction of 293 degrees C or more of boiling points, the velocity constant of the appearance in each reaction temperature was computed noting that the order of reaction of the appearance to the concentration of the fraction of 293 degrees C or more of boiling points was the 2nd order, the Arrhenius plot was taken, and Arrhenius equation was obtained. Based on the obtained Arrhenius equation, the reaction temperature taken to convert the fraction of 293 degrees C or more of boiling points with 60% of the weight of an invert ratio was computed. About the experimental result in each reaction temperature, the invert ratio of the fraction of 293 degrees C or more of boiling points was plotted on the axis of abscissa, the middle-cut yield of the boiling range of 127-293 degrees C of boiling points was plotted on the axis of ordinate, and the approximation curve which shows the relation between an invert ratio and middle-cut yield was obtained. From this approximation curve, the middle-cut yield of the boiling range which is 127-293 degrees C of boiling points in case the invert ratio of the fraction of 293 degrees C or more of boiling points is 60 % of the weight was computed.
[0086]
The middle-cut yield of the boiling range of 127-360 degrees C of boiling points in the reaction temperature which an example takes the fraction of 360 degrees C or more of boiling points shown as an index of the decomposition activity of a catalyst and middle-cut selectivity converting with 60% of the weight of an invert ratio, and its invert ratio is the following, and was made and computed.
[0087]
About the reaction which converts the fraction of 360 degrees C or more of boiling points, the velocity constant of the appearance in each reaction temperature was computed noting that the order of reaction of the appearance to the concentration of the fraction of 360 degrees C or more of boiling points was the 2nd order, the Arrhenius plot was taken, and Arrhenius equation was obtained. Based on the obtained Arrhenius equation, the reaction temperature taken to convert the fraction of 360 degrees C or more of boiling points with 60% of the weight of an invert ratio was computed. About the experimental result in each reaction temperature, the invert ratio of the fraction of 293 degrees C or more of boiling points was plotted on the axis of abscissa, the middle-cut yield of the boiling range of 127-360 degrees C of boiling points was plotted on the axis of ordinate, and the approximation curve which shows the relation between an invert ratio and middle-cut yield was obtained. From this approximation curve, the middle-cut yield of the boiling range which is 127-360 degrees C of boiling points in case the invert ratio of the fraction of 360 degrees C or more of boiling points is 60 % of the weight was computed.
[0088]

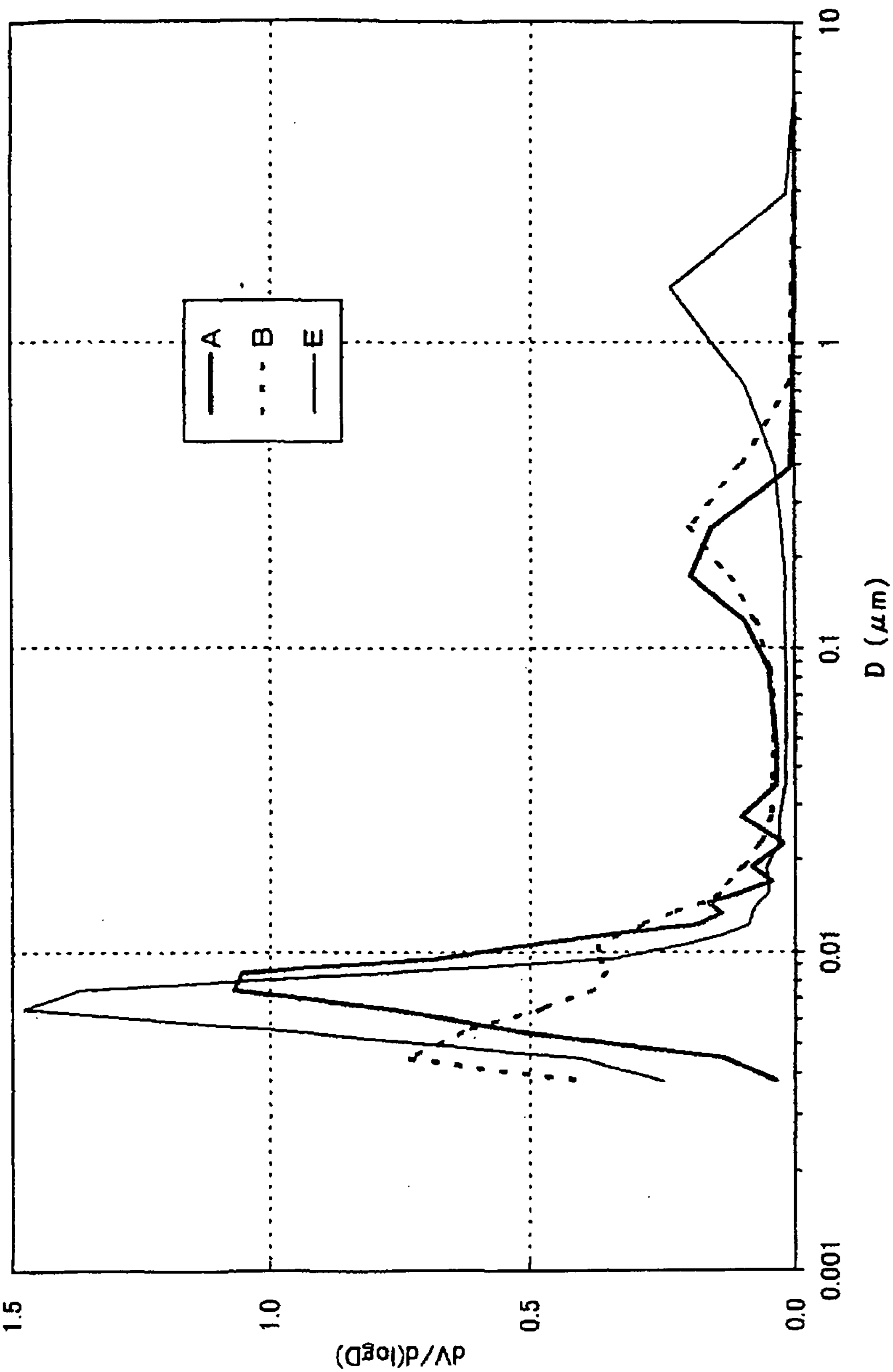
Availability on industry Since the hydrocracking catalyst of this invention has specific pore structure about both meso pore and macro pore, while it has sufficient reinforcement mechanically, it can demonstrate the hydrocarbon oil which contains the fraction which has the boiling point 250 degrees C or more 80% of the weight or more, for example, and the hydrocracking catalyst engine performance in which it excelled to the vacuum gas oil especially, and can attain an efficient hydrocracking reaction.
[Brief Description of the Drawings]
[Drawing 1]
Drawing 1 is a graph which shows the pore volume distribution of the hydrocracking catalyst produced in the example and the example of a comparison of this invention, A and B show among a graph the pore volume distribution of the catalysts A and B produced in the example, E shows the pore volume distribution of the catalyst E produced in the example of a comparison, the axis of ordinate and axis of abscissa of a graph show dV/d (logD) and D, respectively, V is pore volume, and D is a pole diameter.

[Translation done.]

DRAWINGS

[Drawing 1]

Fig. 1



[Translation done.]

(19)日本国特許庁（ＪＰ）　(12)**公表特許公報**（Ａ）　(11)特許出願公表番号

特表2002－523231

（P2002－523231A）

(43)公表日　平成14年7月30日(2002.7.30)

(51)Int.Cl.⁷	識別記号	ＦＩ		テーマコード*(参考)
Ｂ０１Ｊ　23/85		Ｂ０１Ｊ　23/85	Ｍ	４Ｇ０６９
29/16		29/16	Ｍ	４Ｈ０２９
35/10	３０１	35/10	３０１Ａ	
37/00		37/00	Ｈ	
Ｃ１０Ｇ　47/12		Ｃ１０Ｇ　47/12		

審査請求　有　　予備審査請求　未請求(全 33 頁)　　最終頁に続く

(21)出願番号　特願2000－567304(P2000－567304)
(86)(22)出願日　平成11年8月31日(1999.8.31)
(85)翻訳文提出日　平成12年5月1日(2000.5.1)
(86)国際出願番号　ＰＣＴ／ＪＰ９９／０４７２２
(87)国際公開番号　ＷＯ００／１２２１３
(87)国際公開日　平成12年3月9日(2000.3.9)
(31)優先権主張番号　特願平10－246458
(32)優先日　平成10年9月1日(1998.9.1)
(33)優先権主張国　日本（ＪＰ）
(81)指定国　ＥＰ(ＡＴ，ＢＥ，ＣＨ，ＣＹ，ＤＥ，ＤＫ，ＥＳ，ＦＩ，ＦＲ，ＧＢ，ＧＲ，ＩＥ，ＩＴ，ＬＵ，ＭＣ，ＮＬ，ＰＴ，ＳＥ)，ＩＤ，ＪＰ，ＫＲ，ＳＧ，ＵＳ

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(54)【発明の名称】　水素化分解触媒及びその製造方法並びに水素化分解方法

(57)【要約】
水素化分解触媒は、複合酸化物の粒子およびその粒子間に存在するバインダーを有する担体と、周期律表の第６族、第９族および第１０族から選ばれる少なくとも１種の金属成分を担体に担持して有する。触媒は、中央細孔直径が４０～１００Åであり、細孔直径４０～１００Åの範囲の細孔容積が少なくとも０．１ｍL／ｇである。また、触媒の細孔直径０．０５～５μｍの範囲の細孔容積が０．０５～０．５ｍL／ｇであり、且つ細孔直径０．５～１０μｍの細孔容積が０．０５ｍL／ｇ未満である。この触媒は実用的な機械的強度を有し、炭化水素油類、特に減圧軽油の水素化分解反応における転化率および中間留分の選択性が高い。

【特許請求の範囲】

【請求項１】　複合酸化物の粒子およびその粒子間に存在するバインダー部分を有する担体と、上記担体に担持された周期律表の第６族、第９族および第１０族から選ばれる少なくとも１種の金属成分とを有する水素化分解触媒であって、

上記触媒の中央細孔直径が４０～１００Åであり、細孔直径４０～１００Åの範囲の細孔の容積が少なくとも０．１ｍＬ／ｇであり、

上記触媒の細孔直径０．０５～０．５μｍの範囲の細孔の容積が０．０５～０．５ｍＬ／ｇであり且つ細孔直径０．５～１０μｍの細孔の容積が０．０５ｍＬ／ｇ未満である水素化分解触媒。

【請求項２】　上記複合酸化物が、シリカ－アルミナ、シリカ－チタニア、シリカ－ジルコニア、シリカ－マグネシア、シリカ－アルミナ－チタニア及びシリカ－アルミナ－ジルコニアから選ばれる少なくとも１種の複合酸化物から構成される請求項１記載の水素化分解触媒。

【請求項３】　上記複合酸化物が、シリカ－アルミナ、シリカ－チタニア、シリカ－ジルコニア、シリカ－マグネシア、シリカ－アルミナ－チタニア、シリカ－アルミナ－ジルコニアから選ばれる少なくとも１種の複合酸化物と、ＵＳＹゼオライトとから構成される請求項１記載の水素化分解触媒。

【請求項４】　上記バインダー部分が、アルミナ及びボリアーアルミナの少なくとも１種から構成される請求項１～３のいずれか一項に記載の水素化分解触媒。

【請求項５】　上記複合酸化物の粒子の少なくとも６０％は、直径が１０μｍ以下である請求項１～３のいずれか一項に記載の水素化分解触媒。

【請求項６】　２５０℃以上の沸点を有する留分を８０重量％以上含有する炭化水素油を水素化分解するための請求項１に記載の水素化分解触媒。

【請求項７】　バナジウム分及びニッケル分が、それぞれ、０．０００５重量％以下である炭化水素油を水素化分解するための請求項１または６に記載の水素化分解触媒。

【請求項８】　上記炭化水素油が減圧軽油であり、減圧軽油中にバナジウム

分及びニッケル分が、それぞれ、０．０００１重量％以下で含まれる請求項７に記載の水素化分解触媒。

【請求項９】　上記触媒の中央細孔径が、５０～８５Åである請求項１に記載の水素化分解触媒。

【請求項１０】　上記細孔直径４０～１００Åの範囲の細孔の容積が少なくとも０．１５～０．６ｍＬ／ｇである請求項１に記載の水素化分解触媒。

【請求項１１】　上記細孔直径０．０５～０．５μｍの範囲の細孔の容積が０．０５～０．１３ｍＬ／ｇである請求項１、９及び１０のいずれか一項に記載の水素化分解触媒。

【請求項１２】　上記細孔直径０．５～１０μｍの細孔の容積が０．０１ｍＬ／ｇ未満であることを特徴とする請求項１１に記載の水素化分解触媒。

【請求項１３】　請求項１に記載の水素化分解触媒の製造方法であって、

直径が１０μｍ以下の凝集粒子を少なくとも６０重量％含む複合酸化物粉体とバインダーとを混合し、

粉体とバインダーとの混合物を成形、乾燥及び焼成して担体を形成し、

上記担体に周期律表の第６族、第９族および第１０族から選ばれる少なくとも１種の金属成分を担持することを特徴とする水素化分解触媒の製造方法。

【請求項１４】　上記複合酸化物粉体が、シリカ－アルミナ、シリカ－チタニア、シリカ－ジルコニア、シリカ－マグネシア、シリカ－アルミナ－チタニア、シリカ－アルミナ－ジルコニアから選ばれる少なくとも１種から構成される請求項１３に記載の水素化分解触媒の製造方法。

【請求項１５】　上記複合酸化物粉体が、シリカ－アルミナ、シリカ－チタニア、シリカ－ジルコニア、シリカ－マグネシア、シリカ－アルミナ－チタニア、シリカ－アルミナ－ジルコニアから選ばれる少なくとも１種と、ＵＳＹゼオライトとから構成される請求項１３記載の水素化分解触媒の製造方法。

【請求項１６】　上記バインダー成分が、アルミニウム水和酸化物及びボリア含有アルミニウム水和酸化物の少なくとも１種から構成される請求項１３～１５のいずれか一項に記載の水素化分解触媒の製造方法。

【請求項１７】　複合酸化物の中央細孔直径が３５～１００Åの範囲にある

請求項１３～１５のいずれか一項に記載の水素化分解触媒の製造方法。

【請求項１８】　炭化水素油を、水素の存在下で、請求項１に記載の水素化分解触媒に接触させることにより、上記炭化水素油に含まれる相対的に高い沸点を有する留分を減少させた生成物に変換することを特徴とする炭化水素油の水素化分解方法。

【請求項１９】　上記炭化水素油が、２５０℃以上の沸点を有する留分を８０重量％以上含有する炭化水素油であることを特徴とする請求項１８に記載の水素化分解方法。

【請求項２０】　上記炭化水素油中に含まれるバナジウム分及びニッケル分が、それぞれ、０．０００５重量％以下である請求項１８または１９に記載の水素化分解方法。

【請求項２１】　上記炭化水素油が減圧軽油であり、当該減圧軽油に含まれるバナジウム分及びニッケル分が、それぞれ、０．０００１重量％以下である請求項２０に記載の水素化分解方法。

【発明の詳細な説明】

【０００１】

発明の分野

本発明は、炭化水素油の水素化分解方法並びに炭化水素油の水素化分解方法に好適に用いられる触媒及びその製造方法に関する。本発明は、特に、減圧軽油留分を効率よく水素化分解して軽質油に転化せしめることのできる水素化分解方法並びに減圧軽油留分の水素化分解方法に好適に用いられる触媒及びその製造方法に関する。

【０００２】

背景技術

最近の石油類の需要は軽質化傾向にある。ガソリンやナフサに関しては、流動床接触分解によって増産を図ることが可能であるが、中間留分と呼ばれる灯油、軽油、ジェット燃料などは流動床接触分解では好ましい品質のものが得られない。このため、石油精製工業においては、しばしば、高品質な中間留分の増産のために減圧軽油を水素化分解する方法が用いられる。

【０００３】

減圧軽油の水素化分解では、高圧の水素存在下、高温で原料油と触媒を接触させることによって目的の留分を得ることができるが、そのための反応条件と触媒の選定は重要である。例えば、転化率を上げるには、反応条件をより厳しくするか、固体酸性の強いゼオライトをより多く含有する担体に水素化活性金属種を担持した触媒を用いればよい。しかしながら、そのような触媒を用いて反応させると、転化率は高くなるが、ガスやナフサが多量に生成し、中間留分の選択性が悪くなるという欠点がある。

【０００４】

そこで、中間留分を効率よく生産する触媒の設計においては、反応する炭化水素分子の拡散性を考慮して、触媒の細孔径分布に注意が払われる（Julius Scherzer, A. J. Gruia, “HYDROCRACKING SCIENCE AND TECHNOLOGY” Mercel Dekker, Inc., New York, 1996）。例えば、特開平６－１９０２７８号公報では、ボリアとシリカとアルミナから成る担体に水素化活性金属を担持した水素化分解触媒

において、平均細孔直径が９０～１２０Åであるものが高い中間留分選択性を得るのに好適であることが開示されている。このように、いわゆるメソポアの細孔径分布を考慮することによって、中間留分選択性を向上させることはこの分野で知られた技術である。

【０００５】

一方、固定床流通式の反応装置に充填して工業的に用いられる水素化分解触媒は、通常、円柱状や球状に成形したものである。このような成形触媒中に０．０５μｍ以上のいわゆるマクロポアを存在させる技術もまた知られている。例えば、特公平５－３６０９９号公報は、主に常圧残油のような重質炭化水素を水素化処理するために、アルミナ系無機酸化物とゼオライトからなる担体に水素化活性成分を担持させてなる触媒を開示している。この公報では、この触媒が細孔直径６００Å以上のマクロポアを０．１ｍＬ／ｇ以上有するために、炭素質物質や金属汚染物の沈着及びそれによる細孔の閉塞を防止することができ、結果的に灯軽油得率が改善されることが開示されている。

【０００６】

しかしながら、一般に、マクロポアを有する成形触媒は、空隙率が高くなるため機械的強度が低くなり（白崎高保、藤堂尚之編「触媒調製」講談社、1974）、触媒を製造する際、触媒を反応器に充填する際、あるいは反応実施中に触媒が破壊したり粉化したりすることに起因した問題が生じ易いという欠点を有する。本発明者の知る限りにおいて、特定のメソポアの細孔径分布及び特定のマクロポアの細孔径分布を水素化分解触媒に同時に導入して、炭化水素油、好ましくは、所定の沸点以上の留分を主に含むとともに脱金属化された炭化水素油、特に、減圧軽油または重質軽油の水素化分解にかかる水素化分解触媒を使用した技術はこれまでに存在しない。

【０００７】

発明の開示

本発明の目的は、炭化水素油類、特に減圧軽油や重質軽油の水素化分解において転化率および中間留分の選択性が高く、かつ実用的な機械的強度を有する新規な水素化分解触媒及びその製造方法並びにその水素化分解触媒を用いた水素化分

解方法を提供することにある。

【０００８】

本発明の水素化分解触媒は、複合酸化物の粒子およびその粒子間に存在するバインダー部分を有する触媒担体と、周期律表の第６族、第９族および第１０族から選ばれる少なくとも１種の金属成分とを含有する水素化分解触媒であり、（Ａ）該触媒の中央細孔直径が４０～１００Åであり、細孔直径４０～１００Åの範囲の細孔容積が少なくとも０．１ｍＬ／ｇであり；（Ｂ）該触媒の細孔直径０．０５～０．５μｍの範囲の細孔容積が０．０５～０．５ｍＬ／ｇであり、且つ細孔直径０．５～１０μｍの細孔容積が０．０５ｍＬ／ｇ未満であることを特徴とする。

【０００９】

複合酸化物が、シリカ－アルミナ、シリカ－チタニア、シリカ－ジルコニア、シリカ－マグネシア、シリカ－アルミナ－チタニア、シリカ－アルミナ－ジルコニアから選ばれる１種または２種以上から構成される、または、複合酸化物が、シリカ－アルミナ、シリカ－チタニア、シリカ－ジルコニア、シリカ－マグネシア、シリカ－アルミナ－チタニア、シリカ－アルミナ－ジルコニアから選ばれる１種または２種以上とＵＳＹゼオライトとから構成されることが好ましい。

【００１０】

また、バインダー部分が、アルミナ、ボリアーアルミナから選ばれる１種または２種以上から構成され、金属成分が、モリブデン、タングステン、コバルト、ロジウム、イリジウム、ニッケル、パラジウム、白金のうちの１種または２種以上であることが好ましく、さらに、複合酸化物の粒子について、その直径が１０μｍ以下であるものが少なくとも６０％であることが好ましい。

【００１１】

本発明による水素化分解触媒の製造方法は、直径１０μｍ以下の粉体を少なくとも６０％含む複合酸化物粉体とバインダー成分とを混合する工程と、混合物を乾燥及び焼成して担体を形成する工程と、その担体に周期律表の第６族、第９族および第１０族から選ばれる少なくとも１種の金属成分を担持する工程とを含み、それにより、（Ａ）中央細孔直径が４０～１００Åであり、細孔直径４０～１

００Åの範囲の細孔容積が少なくとも０．１ｍＬ／ｇであり、かつ、（Ｂ）細孔直径０．０５～０．５μｍの範囲の細孔容積が０．０５～０．５ｍＬ／ｇであり、細孔直径０．５～１０μｍの細孔容積が０．０５ｍＬ／ｇ未満である水素化分解触媒を得る方法である。

【００１２】

上記方法において、バインダー成分が、アルミニウム水和酸化物、ボリアを含むアルミニウム水和酸化物から選ばれる１種または２種以上から構成されることが好ましい。

【００１３】

本発明に従う炭化水素油の水素化分解方法は、炭化水素油を、水素の存在下で、上述の本発明の水素化分解触媒と接触させることによって、炭化水素油を、その炭化水素油に含まれる相対的に高い沸点を有する留分を減少させた生成物に変換することができる方法である。

【００１４】

発明を実施するための好ましい具体例の説明

以下、本発明の水素化分解触媒及び水素化分解方法の詳細について、触媒の細孔特性、触媒の構成材料、触媒の製造方法及び水素化分解反応などに分けて説明する。

【００１５】

[水素化分解触媒の細孔特性]

本発明に係る水素化分解触媒は、下記（Ａ）、（Ｂ）の両条件を満たす細孔特性を満足することを特徴とする。

（Ａ）中央細孔直径が４０～１００Åであり、細孔直径４０～１００Åの範囲の細孔容積が少なくとも０．１ｍＬ／ｇであること。

（Ｂ）細孔直径０．０５～０．５μｍの範囲の細孔容積が０．０５～０．５ｍＬ／ｇであり、細孔直径０．５～１０μｍの細孔容積の細孔容積が０．０５ｍＬ／ｇ未満であること。

【００１６】

いわゆるメソポアの細孔特性、すなわち上記（Ａ）の条件に関する細孔特性は

、窒素ガス吸着法によって測定され、ＢＪＨ法などによって細孔容積と細孔直径の関係を算出することができる。また、中央細孔直径は、窒素ガス吸着法において相対圧０．９６６７の条件で得られる細孔容積をＶとするとき、細孔直径の大きい側からの累積細孔容積がＶ／２となる細孔直径をいう。水素化分解触媒の中央細孔直径は、４０～１００Åの範囲にあり、さらに、中央細孔直径が４５～９０Åの範囲にあるもの、特には、中央細孔直径が５０～８５Åの範囲にあるものが好ましく用いられる。細孔直径４０～１００Åの範囲の細孔容積が少なくとも０．１ｍＬ／ｇであり、この細孔容積は０．１～１．０ｍＬ／ｇ、特には、０．１５～０．６ｍＬ／ｇであることが好ましい。

【００１７】

水素化分解触の上記メソポアの細孔特性は、基本的には、複合酸化物の細孔特性を上記メソポアの細孔特性を持つように制御することにより得ることができる。これは、通常、複合酸化物のメソポアの細孔特性が複合酸化物により触媒が形成されるまで維持されるからである。

【００１８】

いわゆるマクロポアの細孔特性、すなわち上記（Ｂ）の条件に関する細孔特性は、水銀圧入法を用いて測定でき、水銀の接触角を１４０°、表面張力を４８０ｄｙｎｅｓ／ｃｍとし、全ての細孔は円筒形であると仮定して算出できる。直径０．０５～１μｍの細孔容積が０．０５～０．５ｍＬ/ｇ、直径１μｍ以上の細孔容積が０．０５ｍＬ/ｇ未満である水素化分解触媒が用いられる。さらに、直径０．０５～０．５μｍの細孔容積が０．０４～０．５ｍＬ/ｇ、特には０．０５～０．５ｍＬ/ｇであり、直径１μｍ以上の細孔容積が０．０５ｍＬ/ｇ未満、さらには０．０２ｍＬ／ｇ未満、特には０．０１ｍＬ／ｇであることが触媒の機械的強度を高めるために好ましい。

【００１９】

マクロポアの細孔特性は、複合酸化物粒子間の空隙と空隙のバインダによる充填率とにより制御することができる。複合酸化物粒子間の空隙は、複合酸化物粒子の粒径により制御することができる。上記充填率は、後述するバインダと複合酸化物粒子との混合比または重量比により制御することができる。

【００２０】

メソポアとマクロポアの細孔特性は、また、後述するバインダの性状及び混練条件により影響され得る。

【００２１】

［複合酸化物］

本発明でいう複合酸化物とは、固体酸性を有する複合酸化物である。例えば、二元複合酸化物では、K. Shibata, T. Kiyoura, J. Kitagawa, K. Tanabe, Bull. Chem. Soc. Jpn., 46, 2985 (1973)で酸性発現が確認されているものをはじめ数多くのものが知られているが、シリカ－アルミナ、シリカ－チタニア、シリカ－ジルコニア、シリカ－マグネシアが好ましく用いられる。三元複合酸化物としては、シリカ－アルミナ－チタニア、シリカ－アルミナ－ジルコニアが好ましく用いられる。また、本発明でいう複合酸化物には、ＵＳＹゼオライトなどのゼオライトが含まれ、用いることができる。

【００２２】

ＵＳＹゼオライトとは、超安定Ｙ型ゼオライトのことで、酸処理、高温処理、水蒸気処理などにより、結晶性の劣化に高い抵抗力を有し、アルカリ金属イオンの含有量が４重量％未満、好ましくは１重量％未満で、かつ２４．５０Å未満の格子定数、ならびに５またはそれ以上のシリカ(SiO_2)／アルミナ(Al_2O_3)モル比によって特徴づけられるＹ型ゼオライトである。

【００２３】

ＵＳＹゼオライト以外の複合酸化物について粉体の形態のものを水素化分解触媒製造の原料として用いる場合、細孔直径４０～１００Åの範囲にある細孔の容積が少なくとも０．１ｍＬ／ｇであり、中央細孔直径が３５～１００Åの範囲にあるものを用いると、本発明の水素化分解触媒の細孔特性を得やすく、好ましく用いられる。さらに、中央細孔直径が４０～９０Åの範囲にあるもの、特には、中央細孔直径が４５～８５Åの範囲にあるものが好ましく用いられる。また、上記のような細孔特性を満たしていれば、より比表面積の大きな複合酸化物粉体が好ましく用いられる。具体的には、比表面積が２５０ｍ^2／ｇ以上であるものが好ましく、さらに好ましくは３００ｍ^2／ｇ以上、特には３５０ｍ^2／ｇ以上の

ものが好適に用いられる。

【００２４】

本発明でいう複合酸化物について、粉体の形態のものを用いる場合には、凝集粒子の直径が１０μｍ以下であるものが少なくとも６０％である複合酸化物を用いると、本発明のマクロポア特性を得やすく、十分な機械的強度を有する触媒を得やすいので好ましい。２種以上の複合酸化物の粉体を用いる場合には、その全体について、凝集粒子の直径が１０μｍ以下であるものが少なくとも６０％であればよく、直径が１～１０μｍであるものが６０％以上、特には７０％以上あることが好ましい。凝集粒子の粒径は、水中に分散した粒子群にレーザー光を照射し、その散乱光から求めるなどの方法により測定することができる。また、複合酸化物粉体を、乾式粉砕または湿式粉砕によって凝集粒子の直径が１０μｍ以下であるものが少なくとも６０％となるよう前処理して用いてもよい。複合酸化物の凝集粒子を用いて製造された触媒中には、凝集粒子の大きさとほぼ同じ大きさの粒子として複合酸化物が存在している。

【００２５】

［バインダー部分］

本発明で用いられるバインダー部分は、アルミナ、ボリアーアルミナから選ばれる１種または２種以上から構成されることが好ましい。ここでいうアルミナとは、アルミニウム酸化物、水酸化物および／または水和酸化物であり、ボリアーアルミナとは、ボリアを含むアルミニウム酸化物、水酸化物および／または水和酸化物である。ボリアは、混合物として含まれていてもよいし、固溶体または複合化合物として含まれていてもよい。

【００２６】

担体の原料となるバインダー成分は、アルミニウム水酸化物および／または水和酸化物からなる粉体（以下、単にアルミナ粉体ともいう）特には、擬ベーマイトなどのベーマイト構造を有するアルミニウム水和酸化物を用いることが水素化分解活性や中間留分選択性を向上できるので好ましい。また、バインダー成分は、ボリアを含むアルミニウム水酸化物および／または水和酸化物からなる粉体（以下、単にボリアーアルミナ粉体ともいう）特には、ボリアを含む擬ベーマイト

などのベーマイト構造を有するアルミニウム水和酸化物を用いることが水素化分解活性や中間留分選択性を向上できるので好ましい。

【００２７】

触媒を構成する複合酸化物部分およびバインダー部分の合計重量のうち、バインダー部分の重量は、５～５０重量％、特には、１５～３５重量％とすることが好ましい。この範囲未満では、触媒の機械的強度が低下しやすく、この範囲を超えると相対的に水素化分解活性や中間留分選択性が低下する。複合酸化物としてＵＳＹゼオライトを用いる場合、触媒を構成する複合酸化物部分およびバインダー部分の合計重量のうち、ＵＳＹゼオライト部分の重量は、０．１～３０重量％、特には、０．２～２０重量％とすることが好ましい。この範囲未満では、ＵＳＹゼオライトを用いたことによる分解活性向上効果が発現しにくく、この範囲を超えると相対的に中間留分選択性が低下する。複合酸化物としてシリカ・アルミナを用いる場合、シリカ・アルミナ中、アルミナが１０～６０重量％またはシリカ／アルミナのモル比で１～２０になるように用いる。

【００２８】

［金属成分］

本発明の水素化分解触媒には、第６族、第９族、および第１０族から選ばれる１種または２種以上の金属成分を含む。本発明の触媒に用いられる第６族、第９族、第１０族から選ばれる金属としては、モリブデン、タングステン、コバルト、ロジウム、イリジウム、ニッケル、白金、パラジウムが特に好適に用いられる。これらの金属は１種でも、２種以上を混合したものでも良い。これら金属の添加量は、水素化分解触媒中に占める第６族、第９族、第１０族元素の合計量が０．０５～３５重量％、特には０．１～３０重量％となるように添加することが好ましい。金属としてモリブデンを用いる場合、その添加量は水素化分解触媒中５～２０重量％とすることが好ましい。金属としてタングステンを用いる場合、その添加量は水素化分解触媒中５～３０重量％とすることが好ましい。モリブデンやタングステンの添加量について、上記の範囲より少ないと、水素化分解反応に必要な活性金属の水素化機能が不足し、好ましくない。逆に、上記の範囲より多いと、添加した活性金属成分の凝集が起こりやすく好ましくない。金属としてモ

リブデンまたはタングステンを用いる場合には、コバルトまたはニッケルを添加すると、活性金属の水素化機能が向上し、一層好ましい。その場合のコバルトまたはニッケルの合計添加量は、水素化分解触媒中０．５～１０重量％とすることが好ましい。金属としてロジウム、イリジウム、白金、パラジウムのうちの１種または２種以上を用いる場合、その添加量は０．１～５重量％とすることが好ましい。この範囲未満では、十分な水素化機能が得られず、この範囲を超えると経済的でないため、好ましくない。

【００２９】

［水素化分解触媒の組成］

本発明の水素化分解触媒においては、第６族、第９族、および第１０族の金属元素、ホウ素、炭素、水素、窒素、および酸素を除く元素の組成について、アルミニウム以外の元素の酸化物換算のモル数（例えば、SiO_2、TiO_2、ZrO_2、MgOとしてのモル数）の合計とアルミニウムの酸化物換算のモル数（Al_2O_3としてのモル数）との比が、０．５～１０の範囲、さらには、０．７～７の範囲にあることが好ましい。この範囲未満やこの範囲を超える場合、水素化分解活性、中間留分選択性、または触媒の機械的強度が低下して好ましくない。

【００３０】

［水素化分解触媒の製造方法］

このような成形された触媒は、複合酸化物粉体とバインダー成分を混練し、成形した後、乾燥、焼成して担体を作成し、さらに金属成分を含浸担持した後、乾燥、焼成することによって作製することができるが、所定の細孔特性を有する触媒を作製することができるのであれば、他の方法を用いることもできる。

【００３１】

混練には、一般に触媒調製に用いられている混練機を用いることができる。通常は原料を投入し、水を加えて攪拌羽根で混合するような方法が好適に用いられるが、原料および添加物の投入順序など特に限定はない。混練の際には通常水を加えるが、原料がスラリー状の場合などには特に水を加える必要はない。また、加える液体としては、エタノール、イソプロパノール、アセトン、メチルエチルケトン、メチルイソブチルケトンなどの有機溶媒でもよい。混練時の温度や混練

時間は、原料となる複合酸化物、バインダー成分により異なるが、好ましい細孔構造が得られる条件であれば、特に制限はない。同様に、本発明の触媒の性状が維持される範囲内であれば、硝酸などの酸やアンモニアなどの塩基、クエン酸やエチレングリコールなどの有機化合物、セルロースエーテル類やポリビニルアルコールのような水溶性高分子化合物、セラミックス繊維などを加えて混練しても構わない。

【００３２】

混練後の成形は、一般に触媒調製に用いられている成形方法を用いることができる。特に、ペレット状等の任意の形状に効率よく成形できる、スクリュー式押出機などを用いた押出成形や球状に効率よく成形できるオイルドロップ法による成形が好ましく用いられる。成形物のサイズに特に制限はないが、例えば円柱状のペレットであれば、通常直径０．５～２０mm、長さ０．５～１５mm程度のものを容易に得ることができる。

【００３３】

上記のようにして得られた成形物は、乾燥、焼成処理をすることにより、担体とされる。この焼成処理は、空気または窒素などのガス雰囲気中において３００℃～９００℃の温度で０．１～２０時間焼成することが好ましい。

【００３４】

担体に金属成分を担持する方法に特に制限はないが、スプレー、浸漬などによる含浸法や、イオン交換法等が好適に用いられる。また、担持処理と乾燥処理を繰り返すことにより、より多くの金属成分を担持することができる。担体に金属成分を担持させた水素化分解触媒は、空気または窒素などのガス雰囲気中において３００℃～９００℃の温度で０．１～２０時間焼成することが触媒の活性を高めるために好ましい。

【００３５】

［水素化分解触媒および担体の機械的強度］

水素化分解触媒の機械的強度は、直径１．６mmの円柱ペレットの側面圧壊強度として３ｋｇ以上、より好ましくは４ｋｇ以上が得られる。また、成形担体を作成した後、金属成分を含浸担持して触媒を作成する場合においては、歩留まり

よく触媒を製造するために、成形担体についても十分な機械的強度を有することが好ましいが、本発明における成形担体の機械的強度は、直径１．６ｍｍの円柱ペレットの側面圧壊強度として３ｋｇ以上、より好ましくは４ｋｇ以上が得られる。

【００３６】

［水素化分解反応方法］

本発明による炭化水素油の水素化分解方法は、原料の炭化水素油を、その炭化水素油に含まれる相対的に高い沸点を有する留分を、または、特定の温度よりも高い沸点を有する留分を減少させた生成物に変換するに際し、炭化水素油を水素の存在下で上記のような触媒と接触させることによって行う方法である。

【００３７】

原料として用いることができる炭化水素油に特に制限はないが、２５０℃以上の沸点を有する留分を８０重量％以上含有するものが好ましく用いられる。原料として用いることができる炭化水素油の由来にも特に制限はないが、原油、石炭液化油、オイルシェール、オイルサンドなどから誘導されるものやフィッシャートロプシュ合成油などが好ましく用いられる。原料として用いる炭化水素油は、炭化水素以外の不純物を含むものであっても構わないが、不純物含有量が少ないほうが好ましく、脱硫、脱窒素、脱金属などの水素化精製や脱アスファルトなどの前処理をしたものが好ましく用いられる。特に、メソポア及びマクロポアに金属物質が沈着せずそれにより初期の細孔径が維持されることができる材料が好ましい。具体的には、バナジウム分及びニッケル分のいずれもが０．０００５重量％以下、好ましくは０．０００２重量、一層好ましくは０．０００１重量％の原料油が好ましい。

【００３８】

本発明による炭化水素油の水素化分解方法においては、原料の炭化水素油を、特定の温度よりも高い沸点を有する留分を減少させた生成物に変換するが、ここでいう特定の温度には、所望の目的物に応じて任意の温度を選ぶことができ、１８０℃以上４００℃以下の温度を選ぶことが好ましい。また、原料として用いる炭化水素油は、ここで選ばれた特定の温度以上の沸点を有する留分を５０重量％

以上含有することが好ましく、さらには８０重量％以上、特には９０重量％以上含有することが好ましい。

【００３９】

本発明による炭化水素油の水素化分解方法においては、触媒は、反応器に充填した後、乾燥、還元、硫化などの前処理をして用いられることがある。特に、金属成分として第６族の元素を含む場合は、水素化分解反応に使用する前に硫化処理にかけられることが好ましい。

【００４０】

本発明による炭化水素油の水素化分解方法においては、水素の存在下で水素化分解反応が行われるが、全圧が２ＭＰａ以上３０ＭＰａ以下であるような加圧条件下で実施されることが好ましい。本発明による炭化水素油の水素化分解方法に適した液空間速度（ＬＨＳＶ）は、０．２h^{-1}以上５．０h^{-1}以下であり、特に０．３h^{-1}以上３．０h^{-1}以下が好ましい。本発明による炭化水素油の水素化分解方法に適した水素／原料油供給比は、１００ＮＬ／Ｌ以上５０００ＮＬ／Ｌ以下である。本発明による炭化水素油の水素化分解方法においては、２５０℃以上５００℃以下の温度で反応を行うことが好ましく、特に３００℃以上４５０℃以下で行うことが好ましい。

【００４１】

実施例

以下、本発明の触媒及びその製造方法並びに水素化分解方法を、実施例および比較例を用いて詳細且つ具体的に説明する。

［触媒Ａ］

以下のようにして、Ｗ　１１．０重量％、Ｎｉ　１．０重量％、シリカ－アルミナ　６７．９重量％、アルミナ　１７．０重量％からなる触媒Ａを調製した。

【００４２】

シリカ－アルミナ粉体１１３６ｇ（シリカ／アルミナモル比　７．４、凝集粒径１～１０μｍのもの９３．４重量％、灼熱減量１６．４重量％）および擬ベーマイト粉体３２５ｇ（灼熱減量２７．０重量％）を混練混合し、直径１．６ｍｍの円形開口から押出して円筒形状に成形した。この成形物を１３０℃で１５時間

乾燥し、ついで空気の気流下で、６００℃で１時間焼成することにより、シリカーアルミナ／アルミナ混合系の担体を調製した。この担体の平均側面圧壊強度は、６．３ｋｇであった。

【００４３】

この担体に、メタタングステン酸アンモニウム水溶液をスプレー含浸して、１３０℃で１５時間乾燥した後、硝酸ニッケル水溶液をスプレー含浸して、１３０℃で１５時間乾燥した。ついで、空気の気流下で、５００℃で３０分焼成した。こうして触媒Ａを得た。

【００４４】

この触媒Ａの細孔特性を窒素ガス吸着法で測定したところ、細孔直径４０～１００Åの範囲にある細孔の容積が０．３２８ｍＬ／ｇであり、中央細孔直径は５１Åであった。また、触媒Ａの細孔特性を水銀圧入法で測定した結果、細孔直径０．０５～０．５μｍの範囲にある細孔の容積が０．０８５ｍＬ／ｇ、細孔直径０．５μｍ～１０μｍの細孔容積が０．００１ｍＬ／ｇであった。なお、細孔直径０．０５～１μｍの範囲にある細孔の容積は０．０８６ｍＬ／ｇであり、細孔直径１～１０μｍの範囲にある細孔の容積が０．００１ｍＬ／ｇ未満であることもわかった。

【００４５】

触媒Ａの細孔特性を図１中、ラインＡで示した。細孔直径４０～１００Åの範囲（メソポア）にシャープなピークが現れているとともに、細孔直径０．０５～０．５μｍの範囲（マクロポア）にも顕著なピークが現れていることがわかる。

【００４６】

また、この触媒Ａの平均側面圧壊強度は、５．９ｋｇであった。

【００４７】

［触媒Ｂ］

以下のようにして、Ｗ １６．５重量％、Ｎｉ １．５重量％、シリカーアルミナ ６１．１重量％、ＵＳＹゼオライト ０．８重量％、アルミナ １５．５重量％からなる触媒Ｂを調製した。

【００４８】

シリカーアルミナ粉体１３７２ｇ（シリカ／アルミナモル比　４．４、凝集粒径１～１０μｍのもの９４．４重量％、灼熱減量１６．９重量％）、ＵＳＹゼオライト１６．１ｇ（シリカ／アルミナモル比　３０．３、Ｎａ含有量０．０２重量％、格子定数２４．２９Å、凝集粒径１～１０μｍのもの６７．９重量％、灼熱減量１０．６重量％）、および擬ベーマイト粉体３９５ｇ（灼熱減量２７．０重量％）を混練混合し、直径１．６ｍｍの円形開口から押出して円筒形状に成形した。この成形物を１３０℃で１５時間乾燥し、ついで空気の気流下で、６００℃で１時間焼成することにより、シリカーアルミナ／ＵＳＹゼオライト／アルミナ混合系の担体を調製した。この担体の平均側面圧壊強度は、４．０ｋｇであった。

【００４９】

この担体に、メタタングステン酸アンモニウム水溶液をスプレー含浸して、１３０℃で１５時間乾燥した後、硝酸ニッケル水溶液をスプレー含浸して、１３０℃で１５時間乾燥した。ついで、空気の気流下で、５００℃で３０分焼成した。こうして触媒Ｂを得た。

【００５０】

この触媒Ｂの細孔特性を窒素ガス吸着法で測定したところ、細孔直径４０～１００Åの範囲にある細孔の容積が０．２７９ｍＬ／ｇであり、中央細孔直径は５２Åであった。また、触媒Ｂの細孔特性を水銀圧入法で測定した結果、細孔直径０．０５～０．５μｍの範囲にある細孔の容積が０．１０１ｍＬ／ｇ、細孔直径０．５～１０μｍの範囲にある細孔の容積が０．００４ｍＬ／ｇであった。なお、細孔直径０．０５～１μｍの範囲にある細孔の容積は０．１０４ｍＬ／ｇであり、細孔直径１～１０μｍの範囲にある細孔の容積が０．００１ｍＬ／ｇであることもわかった。

【００５１】

触媒Ｂの細孔特性を図１中、ラインＢで示した。触媒Ａと同様に、細孔直径４０～１００Åの範囲（メソポア）にシャープなピークが現れているとともに、細孔直径０．０５～０．５μｍの範囲（マクロポア）にも顕著なピークが現れていることがわかる。

【００５２】

触媒Ｂの平均側面圧壊強度は、４．４ｋｇであった。

【００５３】

［触媒Ｃ］

以下のようにして、Ｗ　２２．０重量％、Ｎｉ　２．０重量％、シリカ－アルミナ　５０．９重量％、ＵＳＹゼオライト　４．９重量％、ボリア－アルミナ　１３．９重量％からなる触媒Ｃを調製した。

【００５４】

シリカ－アルミナ粉体１１３６ｇ（シリカ／アルミナモル比　７．４、凝集粒径１～１０μｍのもの９３．４重量％、灼熱減量１６．４重量％）、ＵＳＹゼオライト１０２ｇ（シリカ／アルミナモル比　３０．３、Ｎａ含有量０．０２重量％、格子定数２４．２９Å、凝集粒径１～１０μｍのもの６７．９重量％、灼熱減量１０．６重量％）、およびボリア－アルミナ粉体３２４ｇ（ホウ素含有量２．６重量％、灼熱減量１９．７重量％）を混練混合し、直径１．６ｍｍの円形開口から押出して円筒形状に成形した。この成形物を１３０℃で１５時間乾燥し、ついで空気の気流下で、６００℃で１時間焼成することにより、シリカ－アルミナ／ＵＳＹゼオライト／ボリア－アルミナ混合系の担体を調製した。この担体の平均側面圧壊強度は、６．６ｋｇであった。

【００５５】

この担体に、メタタングステン酸アンモニウム水溶液をスプレー含浸して、１３０℃で１５時間乾燥した後、硝酸ニッケル水溶液をスプレー含浸して、１３０℃で１５時間乾燥した。ついで、空気の気流下で、５００℃で３０分焼成した。こうして触媒Ｃを得た。

【００５６】

この触媒Ｃの細孔特性を窒素ガス吸着法で測定したところ、細孔直径４０～１００Åの範囲にある細孔の容積が０．１９４ｍＬ／ｇであり、中央細孔直径は６９Åであった。また、触媒Ｃの細孔特性を水銀圧入法で測定した結果、細孔直径０．０５～０．５μｍの範囲にある細孔の容積が０．０７６ｍＬ／ｇであり、細孔直径０．５～１０μｍの細孔の容積が０．００１ｍＬ／ｇであった。この触媒

Ｃの平均側面圧壊強度は、８．４ｋｇであった。

【００５７】

［触媒Ｄ］

以下のようにして、Ｗ　２２．０重量％、Ｎｉ　２．０重量％、シリカ－アルミナ　５３．３重量％、ＵＳＹゼオライト　２．４重量％、アルミナ　１３．９重量％からなる触媒Ｄを調製した。

【００５８】

シリカ－アルミナ粉体１１４３ｇ（シリカ／アルミナモル比　４．４、凝集粒径１～１０μｍのもの９4．４重量％、灼熱減量１６．９重量％）、ＵＳＹゼオライト４９ｇ（シリカ／アルミナモル比　３０．３、Ｎａ含有量０．０２重量％、格子定数２４．２９Å、凝集粒径１～１０μｍのもの６７．９重量％、灼熱減量１０．６重量％）、および擬ベーマイト粉体３４０ｇ（灼熱減量２７．０重量％）を混練混合し、直径１．６ｍｍの円形開口から押出して円筒形状に成形した。この成形物を１３０℃で１５時間乾燥し、ついで空気の気流下で、６００℃で１時間焼成することにより、シリカ－アルミナ／ＵＳＹゼオライト／アルミナ混合系の担体を調製した。この担体の平均側面圧壊強度は、４．０ｋｇであった。

【００５９】

この担体に、メタタングステン酸アンモニウム水溶液をスプレー含浸して、１３０℃で１５時間乾燥した後、硝酸ニッケル水溶液をスプレー含浸して、１３０℃で１５時間乾燥した。ついで、空気の気流下で、５００℃で３０分焼成した。こうして触媒Ｄを得た。

【００６０】

この触媒Ｄの細孔特性を窒素ガス吸着法で測定したところ、細孔直径４０～１００Åの範囲にある細孔の容積が０．２３１ｍＬ／ｇであり、中央細孔直径が５２Åであった。また、この触媒Ｄの細孔特性を水銀圧入法で測定した結果、細孔直径０．０５～０．５μｍの範囲にある細孔の容積が０．０７０ｍＬ／ｇ、細孔直径０．５～１０μｍ以上の細孔容積が０．００３ｍＬ／ｇであった。なお、細孔直径０．０５～１μｍの範囲にある細孔の容積が０．０７２ｍＬ／ｇであり、細孔直径１～１０μｍの範囲にある細孔の容積が０．００１ｍＬ／ｇであった。

【００６１】

この触媒Ｄの平均側面圧壊強度は、４．７ｋｇであった。

【００６２】

［触媒Ａおよび触媒Ｂを用いた水素化分解反応］

評価方法１：

触媒充填量１００ｍＬの固定床流通式反応装置に触媒Ａを充填し、予備硫化した後、１５℃での密度０．８３１ｇ／ｍＬ、初留点２６２．９℃、沸点２９３℃以上の留分が９７．８重量％、全硫黄濃度０．００１重量％未満、全窒素濃度０．０００１重量％未満、バナジウム濃度０．０００１重量％未満、ニッケル濃度０．０００１重量未満である減圧軽油を用い、圧力１５ＭＰａ、水素／原料油供給比８００ＮＬ／Ｌ、ＬＨＳＶ＝１．３６h^{-1}、反応温度３９０、３８０、３７０、３６０℃の反応条件で水素化分解反応を行い、沸点２９３℃以上の留分を６０重量％の転化率で転化するのに要する反応温度とその転化率での沸点１２７～２９３℃の沸点範囲の中間留分収率を求めたところ、それぞれ、３７６．４℃、３９．９重量％であった。

【００６３】

同様の反応装置に触媒Ｂを充填して上記と同様の条件で水素化分解反応を行って沸点２９３℃以上の留分を６０重量％の転化率で転化するのに要する反応温度とその転化率での沸点１２７～２９３℃の沸点範囲の中間留分収率を求めたところ、それぞれ３６７．７℃、４０．３重量％であった。

【００６４】

評価方法２：

また、触媒Ａについて上記とは異なる条件で以下のような評価を行った。上記固定床流通式反応装置に触媒Ａを充填し、上記と同じ減圧軽油を用い、圧力１５ＭＰａ、水素／原料油供給比８００ＮＬ／Ｌ、ＬＨＳＶ＝１．３６h^{-1}、反応温度３８０℃の反応条件で水素化分解反応を行い、沸点２９３℃以上の留分の転化率及び沸点１２７～２９３℃の沸点範囲の中間留分収率を求めたところ、それぞれ６４．５重量％及び６４．４重量％であることがわかった。

【００６５】

上記固定床流通式反応装置に触媒Ｂを充填し、上記と同じ減圧軽油を用い、圧力１５ＭＰａ、水素／原料油供給比８００ＮＬ／Ｌ、ＬＨＳＶ＝１．３６／h^{-1}、反応温度３８０℃の反応条件で水素化分解反応を行い、沸点２９３℃以上の留分の転化率及び沸点１２７～２９３℃の沸点範囲の中間留分収率を求めたところ、それぞれ７９．２重量％及び４８．９重量％であることがわかった。

【００６６】

［触媒Ｃおよび触媒Ｄを用いた水素化分解反応］

評価方法１：

触媒充填量１００ｍＬの固定床流通式反応装置に触媒Ｃを充填し、予備硫化した後、１５℃での密度０．９０６０ｇ／ｍＬ、初留点３０９．３℃、沸点３６０℃以上の留分９１．３重量％、全硫黄濃度０．４６重量％、全窒素濃度０．０８１重量％、バナジウム濃度０．０００１重量％未満、ニッケル濃度０．０００１重量％未満である減圧軽油を用い、圧力１５ＭＰａ、水素／原料油供給比１０００ＮＬ／Ｌ、ＬＨＳＶ＝１．３６h^{-1}、反応温度４２０、４１０、４００℃の反応条件で水素化分解反応を行い、沸点３６０℃以上の留分を６０重量％の転化率で転化するのに要する反応温度とその転化率での沸点１２７～３６０℃の沸点範囲の中間留分収率を求めたところ、それぞれ４１０．０℃、４１．２重量％、であった。

【００６７】

同様の反応装置に触媒Ｄを充填して上記と同様の条件で水素化分解反応を行って沸点３６０℃以上の留分を６０重量％の転化率で転化するのに要する反応温度とその転化率での沸点１２７～３６０℃の沸点範囲の中間留分収率を求めたところ、それぞれ４１１．９℃及び４５．６重量％であった。

【００６８】

評価方法２：

また、触媒Ｃ及びＤについて上記評価条件とは異なる条件で以下のような評価試験を行った。

【００６９】

上記固定床流通式反応装置に触媒Ｃを充填し、上記と同じ減圧軽油を用い、圧

力１５ＭＰａ、水素／原料油供給比１０００ＮＬ／Ｌ、ＬＨＳＶ＝１．３６h^{-1}、反応温度４００℃の反応条件で水素化分解反応を行い、沸点３６０℃以上の留分の転化率及び沸点１２７～３６０℃の沸点範囲の中間留分収率を求めたところ、それぞれ４０．９重量％及び７２．４重量％であることがわかった。

【００７０】

また、上記固定床流通式反応装置に触媒Ｄを充填し、上記と同じ減圧軽油を用い、圧力１５ＭＰａ、水素／原料油供給比１０００ＮＬ／Ｌ、ＬＨＳＶ＝１．３６h^{-1}、反応温度４００℃の反応条件で水素化分解反応を行い、沸点３６０℃以上の留分の転化率及び沸点１２７～３６０℃の沸点範囲の中間留分収率を求めたところ、それぞれ３９．４重量％及び８１．３重量％であることがわかった。

【００７１】

比較例

[触媒Ｅ]

以下のようにして、Ｗ　１１．０重量％、Ｎｉ　１．０重量％、シリカ－アルミナ　６７．９重量％、アルミナ　１７．０重量％からなる触媒Ｅを調製した。

【００７２】

シリカ－アルミナ粉体１１３７ｇ（シリカ／アルミナモル比　４．１、凝集粒径１～１０μｍのもの３４．４重量％、灼熱減量２３．９重量％）および擬ベーマイト粉体２９６ｇ（灼熱減量２７．０重量％）を混練混合し、直径１．６ｍｍの円形開口から押出して円筒形状に成形した。この成形物を１３０℃で１５時間乾燥し、ついで空気の気流下で、６００℃で１時間焼成することにより、シリカ－アルミナ／アルミナ混合系の担体を調製した。この担体の平均側面圧壊強度は、２．１ｋｇであった。この担体に、メタタングステン酸アンモニウム水溶液をスプレー含浸して、１３０℃で１５時間乾燥した後、硝酸ニッケル水溶液をスプレー含浸して、１３０℃で１５時間乾燥した。ついで、空気の気流下で、５００℃で３０分焼成した。こうして触媒Ｅを得た。

【００７３】

この触媒Ｅの細孔特性を窒素ガス吸着法で測定したところ、細孔直径４０～１００Åの範囲にある細孔の容積が０．４４２ｍＬ／ｇであり、中央細孔直径は６

２Åであった。また、この触媒Ｅの細孔特性を水銀圧入法で測定した結果、細孔直径０．０５～０．５μｍの範囲にある細孔の容積が０．０２６ｍＬ／ｇであり、細孔直径０．５～１０μｍ以上の細孔容積が０．１０５ｍＬ／ｇであった。なお、細孔直径０．０５～１μｍの範囲にある細孔の容積が０．０５３ｍＬ／ｇであり、細孔直径１～１０μｍの範囲にある細孔の容積が０．０７８ｍＬ／ｇであった。

【００７４】

触媒Ｅの細孔特性を図１中、ラインＥで示した。触媒Ａと同様に、細孔直径４０～１００Åの範囲（メソポア）にシャープなピークが現れている。しかしながら、触媒Ａ及びＢとは異なり、マクロポアのピークは細孔直径１μｍを超える領域に現れている。

【００７５】

この触媒Ｅの平均側面圧壊強度は、３．２ｋｇであった。

【００７６】

［触媒Ｅを用いた水素化分解反応］

評価方法１：

触媒充填量１００ｍＬの固定床流通式反応装置に触媒Ｅを充填し、触媒Ａおよび触媒Ｂについて行った評価方法１と同様の条件で水素化分解反応を行い、沸点２９３℃以上の留分を６０重量％の転化率で転化するのに要する反応温度及びその転化率での沸点１２７～２９３℃の沸点範囲の中間留分収率を求めたところ、それぞれ、３７８．８℃及び３７．０重量％であった。

【００７７】

評価方法２：

触媒充填量１００ｍＬの固定床流通式反応装置に触媒Ｅを充填し、触媒Ａについて行った評価方法２の同様の条件で水素化分解反応を行い、沸点２９３℃以上の留分の転化率、及び沸点１２７～２９３℃の沸点範囲の中間留分収率を求めたところ、それぞれ、５９．６重量％及び６１．０重量％であった。

【００７８】

上記実施例および比較例で用いた測定装置及び方法を以下に記載する。

【００７９】

［凝集粒子の粒度分布測定方法］

日機装（株）ＭＩＣＲＯＴＲＡＣ粒度分析計を用い、湿式測定法で測定した。これは、粉体を水中に分散させ、流れる凝集粒子群にレーザー光を照射し、その前方散乱光により粒度分析を行うものである。

【００８０】

［細孔特性の測定方法］

水銀圧入法による細孔特性の測定には、Ｍｉｃｒｏｍｅｒｉｔｉｃｓ社製ＡｕｔｏＰｏｒｅ９２００型測定器を用いた。窒素ガス吸着法による細孔特性の測定には、Ｍｉｃｒｏｍｅｒｉｔｉｃｓ社製ＡＳＡＰ２４００型測定器を用いた。

【００８１】

［平均側面圧壊強度の測定方法］

富山産業（株）製ＴＨ－２０３ＣＰ錠剤破壊強度測定器を用い、円柱状に押出成形し、乾燥、焼成したサンプルを用いて側面圧壊強度を測定した。測定プローブは先端が直径５ｍｍの円形状のものを使用した。測定サンプルを、円柱サンプルの側面中央に当てて測定する操作を２０回繰り返し、その平均値を算出した。

【００８２】

［転化率、中間留分収率の定義］

実施例および比較例での触媒の活性を示す転化率及び中間留分選択率は、以下のように定義した。

【００８３】

沸点２９３℃以上の留分の転化率＝［１－（生成油中に占める沸点２９３℃以上の留分の重量％／原料油中に占める沸点２９３℃以上の留分の重量％）］×１００（重量％）

沸点３６０℃以上の留分の転化率＝［１－（生成油中に占める沸点３６０℃以上の留分の重量％／原料油中に占める沸点３６０℃以上の留分の重量％）］×１００（重量％）

沸点１２７～２９３℃の沸点範囲の中間留分収率＝［（生成物中の沸点１２７～２９３℃の沸点範囲の留分の重量）／（硫化水素およびアンモニアを除く生成

物の重量）］×１００（重量％）
沸点１２７～３６０℃の沸点範囲の中間留分収率＝［（生成物中の沸点１２７～３６０℃の沸点範囲の留分の重量）／（硫化水素およびアンモニアを除く生成物の重量）］×１００（重量％）

【００８４】

［分解活性、中間留分選択性の指標］

実施例および比較例で触媒の分解活性および中間留分選択性の指標として示している沸点２９３℃以上の留分を６０重量％の転化率で転化するのに要する反応温度とその転化率での沸点１２７～２９３℃の沸点範囲の中間留分収率は、以下のようにして算出した。

【００８５】

沸点２９３℃以上の留分を転化する反応について、沸点２９３℃以上の留分の濃度に対する見かけの反応次数が２次であるとして各反応温度での見かけの反応速度定数を算出して、そのアレニウスプロットをとり、アレニウス式を得た。得られたアレニウス式に基づき、沸点２９３℃以上の留分を６０重量％の転化率で転化するのに要する反応温度を算出した。各反応温度での実験結果について、沸点２９３℃以上の留分の転化率を横軸に、沸点１２７～２９３℃の沸点範囲の中間留分収率を縦軸にプロットして、転化率と中間留分収率の関係を示す近似曲線を得た。この近似曲線より、沸点２９３℃以上の留分の転化率が６０重量％のときの沸点１２７～２９３℃の沸点範囲の中間留分収率を算出した。

【００８６】

実施例で触媒の分解活性および中間留分選択性の指標として示している沸点３６０℃以上の留分を６０重量％の転化率で転化するのに要する反応温度とその転化率での沸点１２７～３６０℃の沸点範囲の中間留分収率は、以下のようにして算出した。

【００８７】

沸点３６０℃以上の留分を転化する反応について、沸点３６０℃以上の留分の濃度に対する見かけの反応次数が２次であるとして各反応温度での見かけの反応速度定数を算出して、そのアレニウスプロットをとり、アレニウス式を得た。得

られたアレニウス式に基づき、沸点３６０℃以上の留分を６０重量％の転化率で転化するのに要する反応温度を算出した。各反応温度での実験結果について、沸点２９３℃以上の留分の転化率を横軸に、沸点１２７～３６０℃の沸点範囲の中間留分収率を縦軸にプロットして、転化率と中間留分収率の関係を示す近似曲線を得た。この近似曲線より、沸点３６０℃以上の留分の転化率が６０重量％のときの沸点１２７～３６０℃の沸点範囲の中間留分収率を算出した。

【００８８】

産業上の利用可能性

本発明の水素化分解触媒は、メソポアおよびマクロポアの両方について特定の細孔構造を有するため、機械的に十分な強度を有すると同時に、例えば、２５０℃以上の沸点を有する留分を８０重量％以上含有する炭化水素油、特に、減圧軽油に対して優れた水素化分解触媒性能を発揮し、効率的な水素化分解反応を達成することができる。

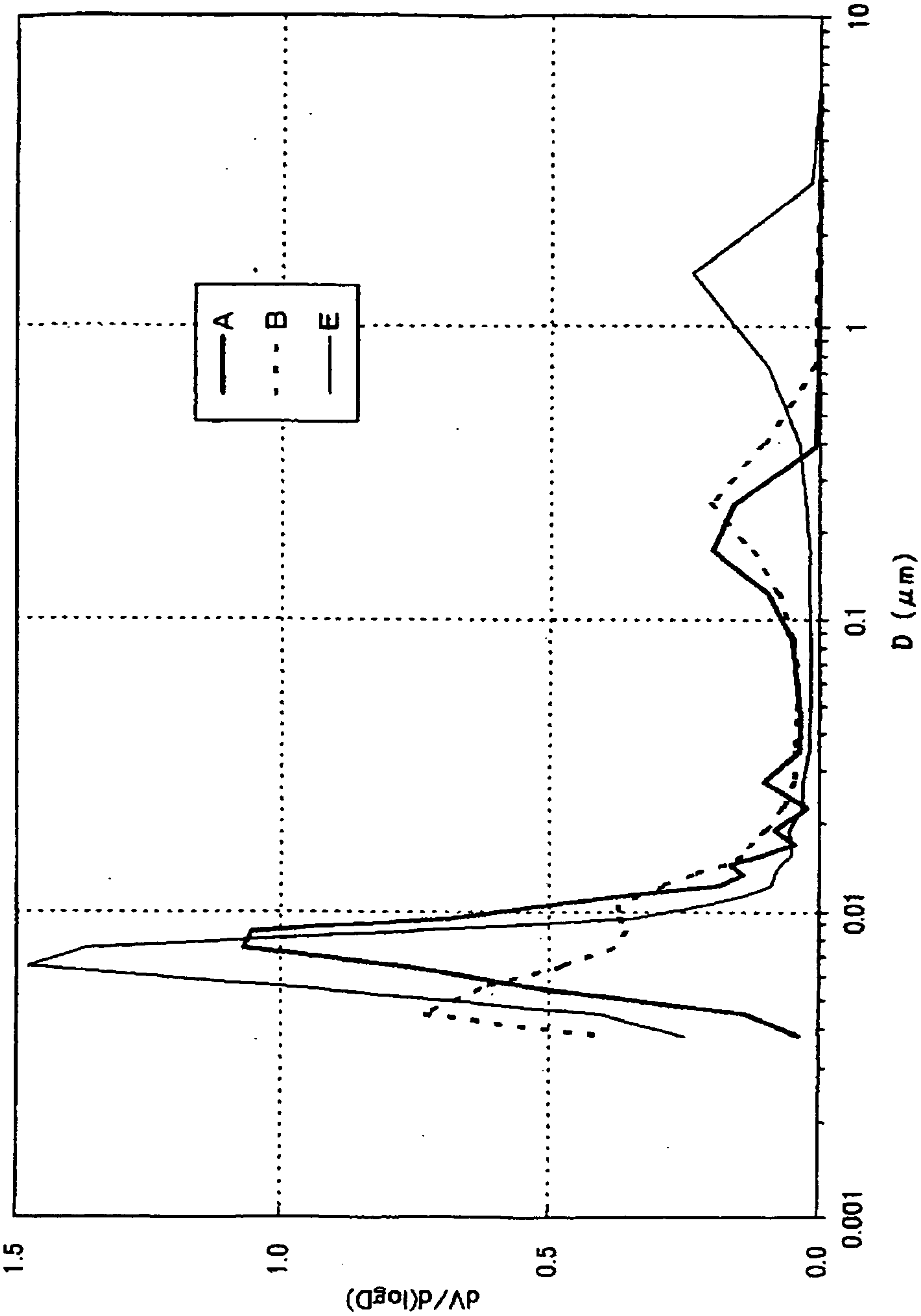
【図面の簡単な説明】

【図１】

図１は、本発明の実施例及び比較例で作製した水素化分解触媒の細孔径分布を示すグラフであり、グラフ中、Ａ及びＢは実施例で作製した触媒Ａ及びＢの細孔径分布を示し、Ｅは比較例で作製した触媒Ｅの細孔径分布を示し、グラフの縦軸及び横軸はそれぞれｄＶ／ｄ（ｌｏｇＤ）及びＤをそれぞれ示し、Ｖは細孔容積であり、Ｄは細孔径である。

【図１】

Ｆｉｇ．１



【国際調査報告】

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 99/04722

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J35/10 C10G47/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
3 December 1999	14/12/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Michiels, P

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International Application No
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(51)Int.Cl.⁷　識別記号　ＦＩ　テーマコード(参考)
Ｃ１０Ｇ 47/14　Ｃ１０Ｇ 47/14

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BA01B BA02A BA03A BA03B
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BC75A BD02A BD02B BD03A
BD03B CC05 EA02Y EB18Y
EC06X EC06Y EC14X EC14Y
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4H029 CA00 DA00